

Novel Electrodes for Low-Temperature SOFCs

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DOE Project Manager: Dr. Lane Wilson

Outline

- **Introduction**
- **Objectives**
- **Technical Approach**
- **Cathode Development**

Intrinsic Catalytic Properties

Architecture: Functionally Graded Electrodes

- **Anode Developments**

Microstructure/Fabrication Processes

Types of Fuels

Pre-reforming

- **Summary**

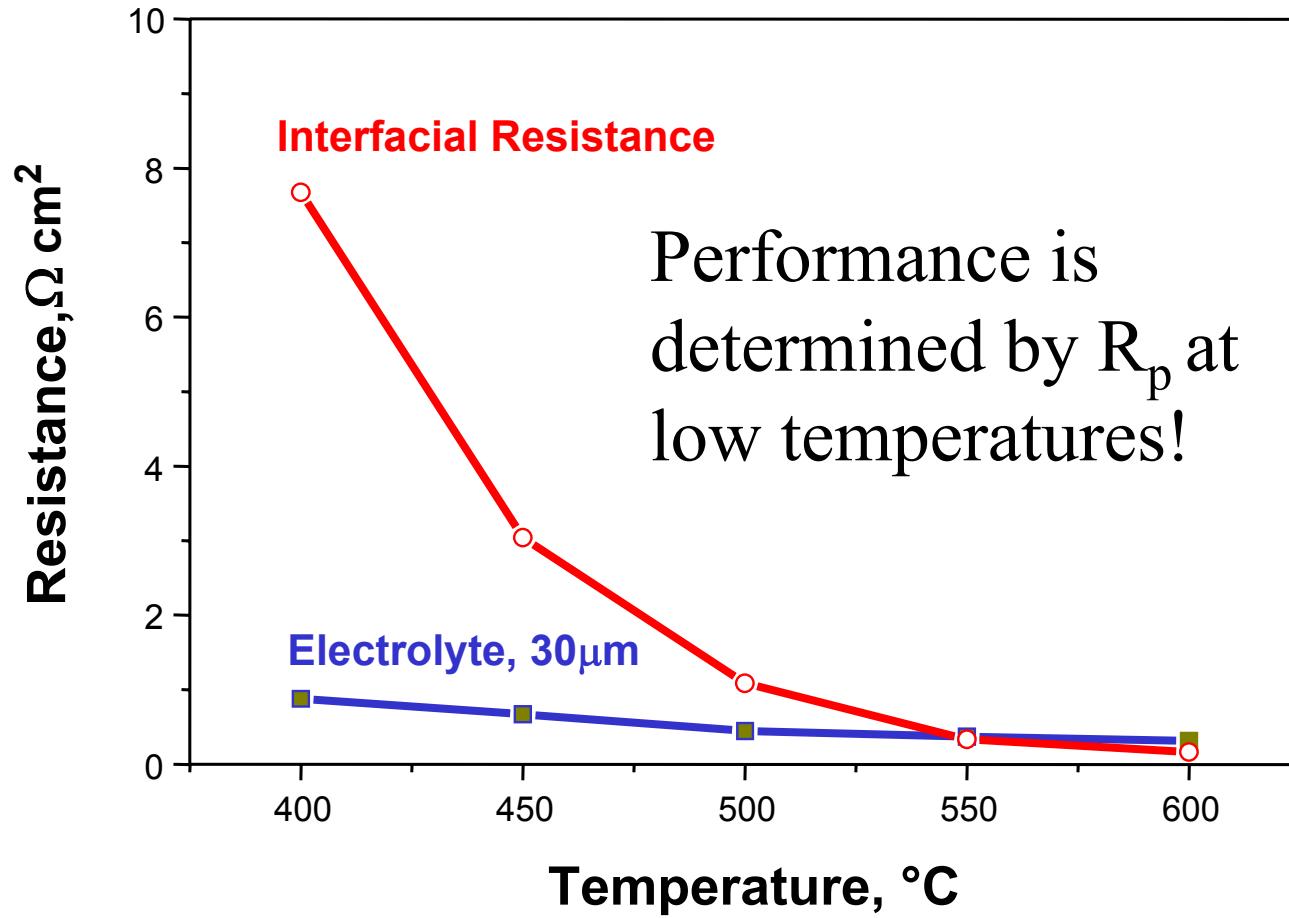
Advantages of SOFCs

The **cleanest, most efficient & versatile** system
for chemical to electrical energy conversion

Challenge: Cost Reduction

- Lower operating temp
 - Much less expensive materials for interconnect etc...
 - Longer operational life
 - Greater probability for mobile applications
- Simple & cost-effective fabrication processes

R_p Increases Rapidly as Temperature is Reduced



Project Objectives

- To gain a profound understanding of electrode reaction mechanisms in SOFCs,
- To rationally design efficient electrodes for low-temperature SOFCs, and
- To fabricate high-performance SOFCs for low-temperature operation.

Technical Approach

Patterned Electrodes

- Reaction Pathway
- Active sites

Modeling

- Transport in Porous Media
 - Active Reaction Sites
 - Reaction Pathways
 - Mechanism

In-situ Characterization

- FTIR, Raman, IS, GC/MS
 - Reaction Mechanism
 - Catalytic Properties

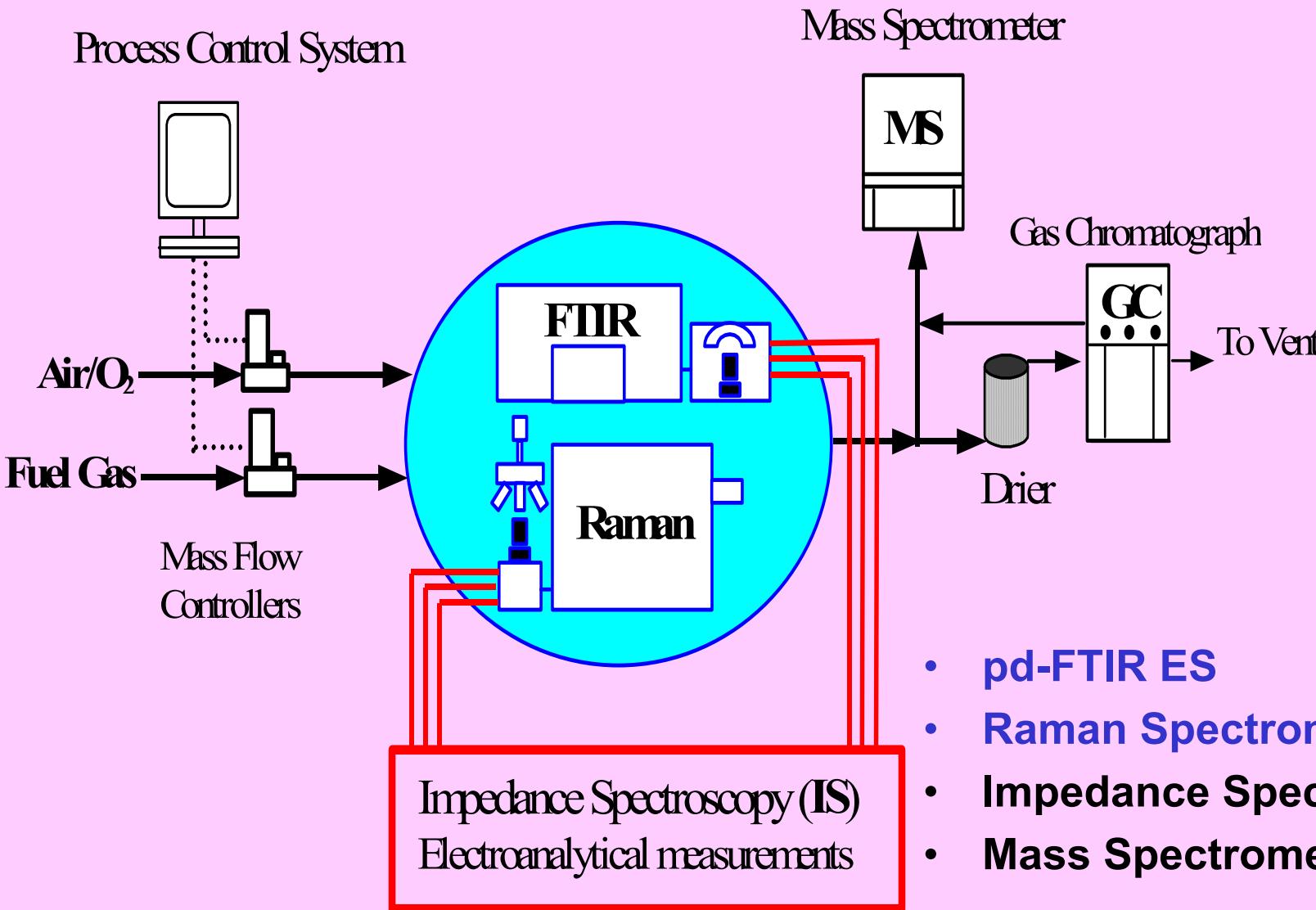
Fabrication of FGE

- Optimal Microstructure
- Graded in Composition
- Cost-effective/Reproducible

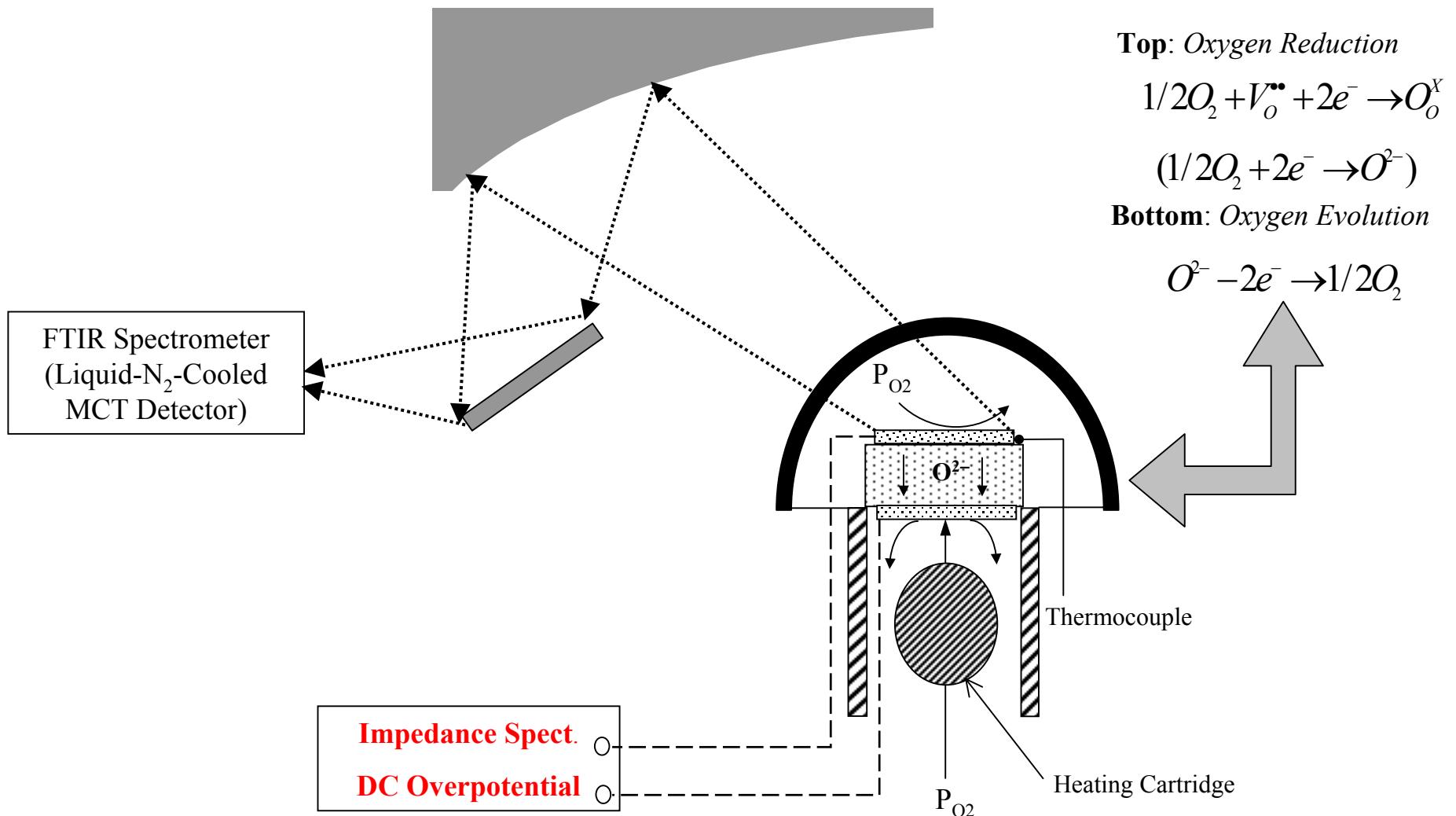
SOFC Performance

- High Performance
- Long-Term Stability

Simultaneously Performing Several Measurements

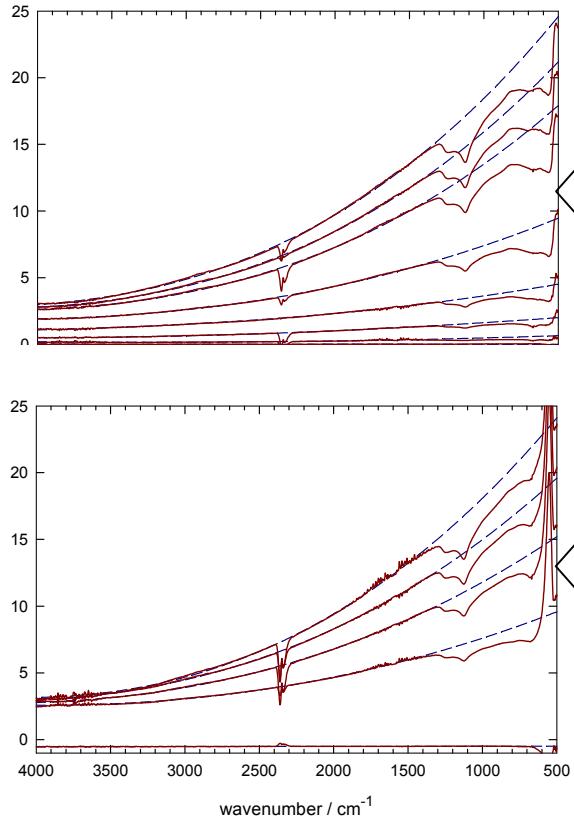


Optical Configuration for *In-Situ* Potential Dependent FTIR-ES

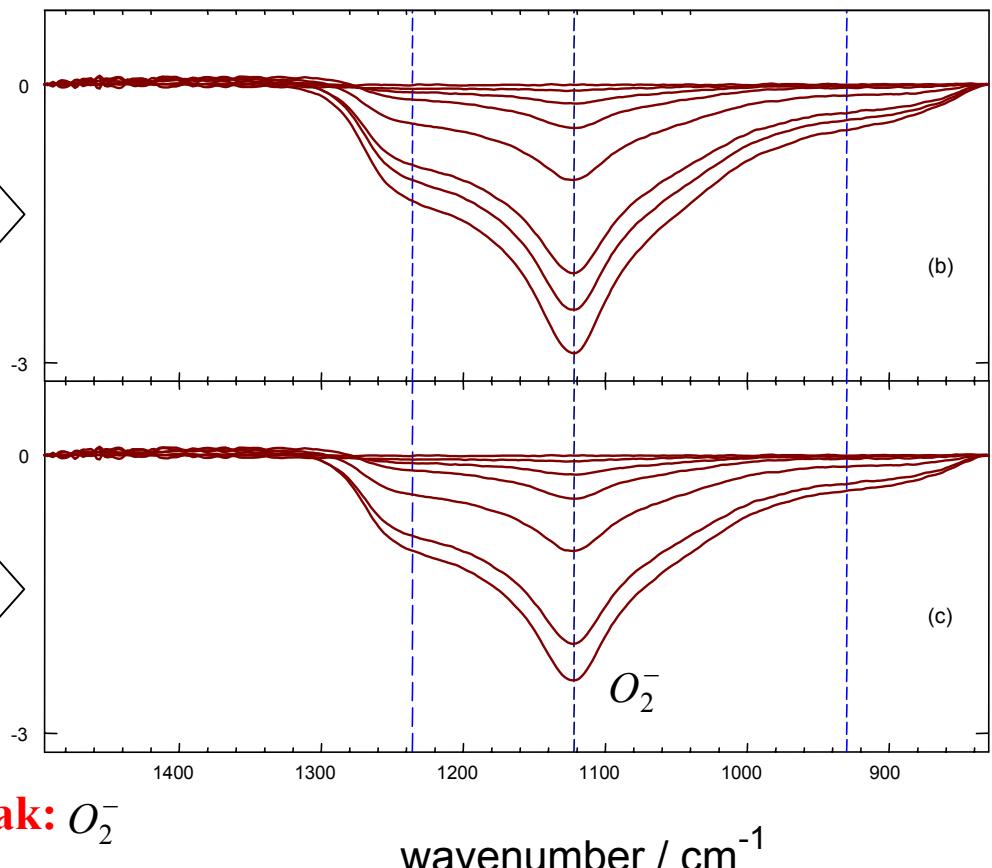


Intermediate Species at the Surface

In-Situ pd-FTIRES Spectra



After local baseline correction



1124 cm^{-1} peak: O_2^-

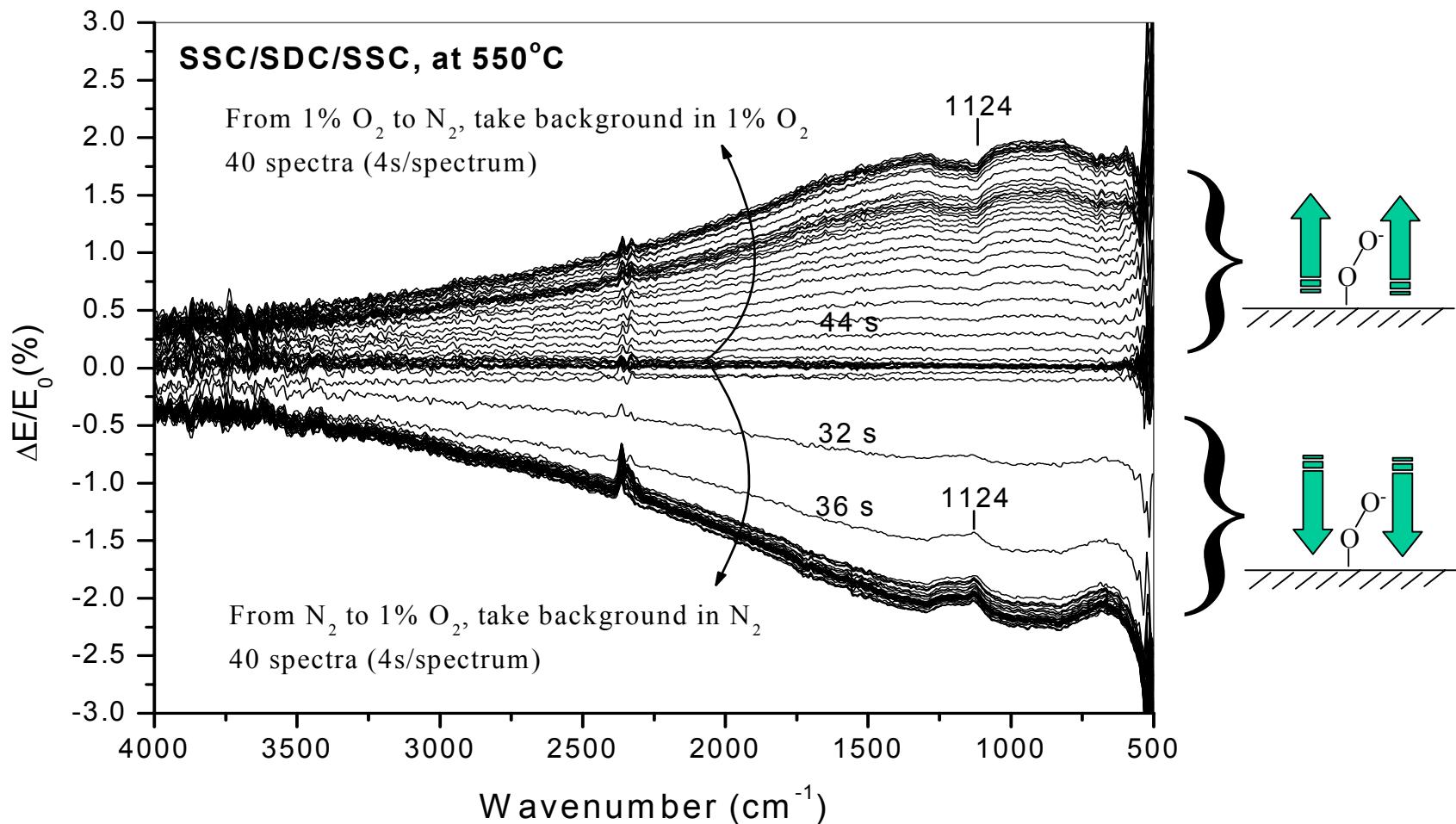
1236 cm^{-1} peak: perturbed O_2^-

930 cm^{-1} peak: O_2^{2-}

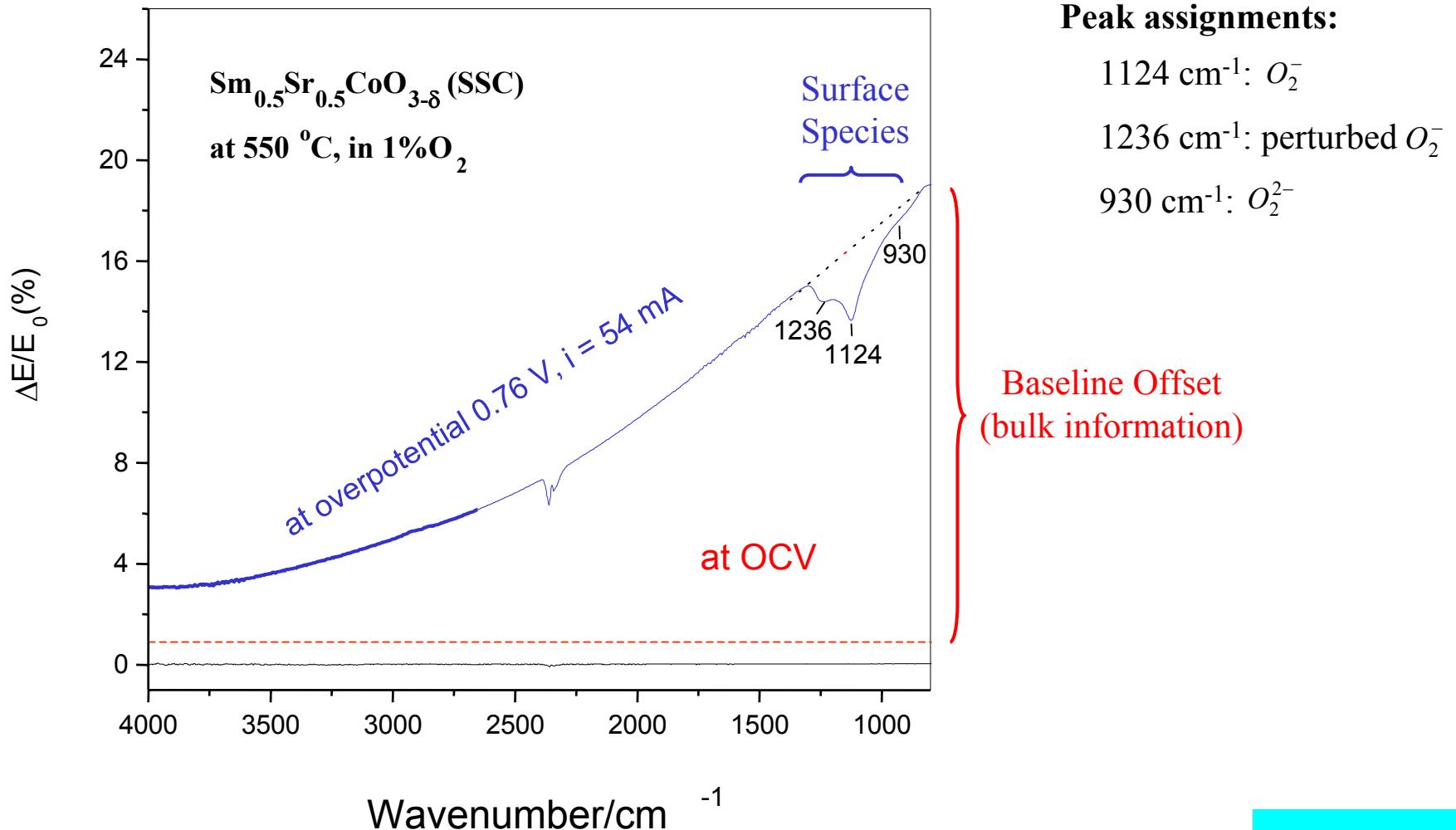
wavenumber / cm^{-1}

Gas switching effect

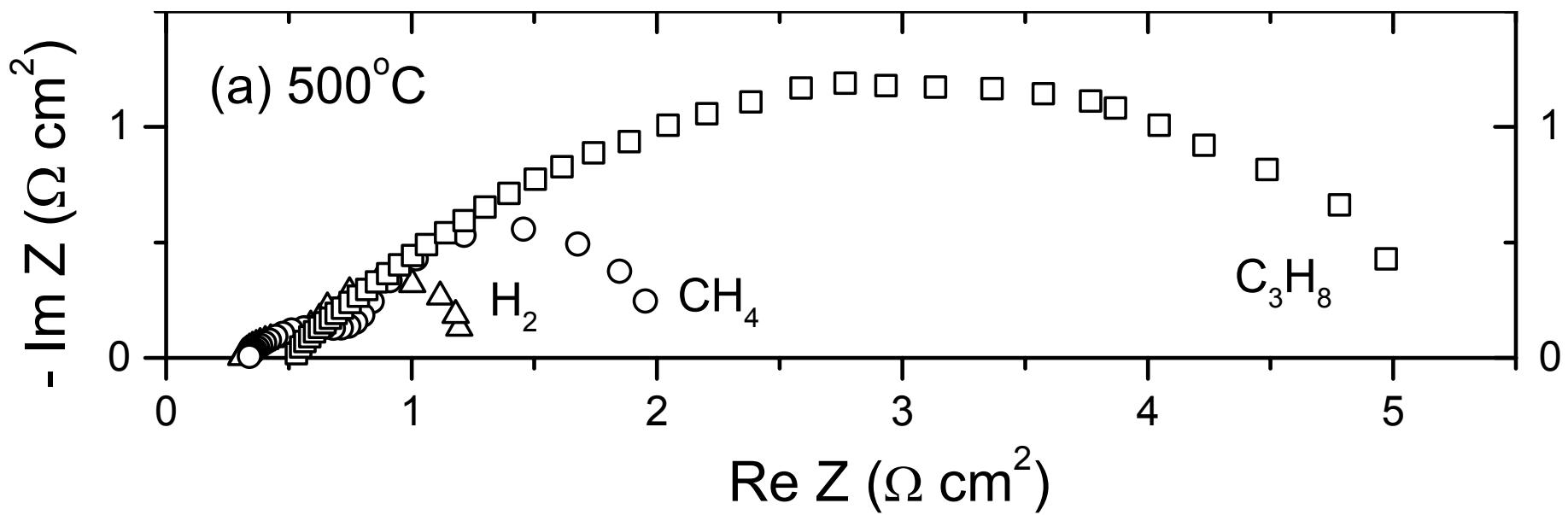
*From N_2 to 1% O_2 and from 1% O_2 to N_2 by fast collecting
(4s/spectrum).*



FTIRES Spectra of SSC: *Surface and Bulk Effect*



Interfacial Resistances to Oxidation of Fuels (H_2 , CH_4 , C_3H_8)



Interfacial resistances increase dramatically (~5 times) when the fuel is switched from H_2 to hydrocarbons

When Hydrogen Is Used as Fuel

Anodic Reaction:



When Propane Is Used as Fuel

- Cracking: $C_3H_8 \rightarrow 3C + 4H_2$
 - Partial oxidation: $C_3H_8 + \frac{3}{2}O_2 \rightarrow 3CO + 4H_2$
 - Steam reforming: $C_3H_8 + 3H_2O \xrightarrow{\Delta} 3CO + 7H_2$
 - CO₂ reforming: $C_3H_8 + 3CO_2 \xrightarrow{\Delta} 6CO + 4H_2$
 - Water shift: $CO + H_2O \rightarrow CO_2 + H_2$
 - Carbon deposition: $2CO \rightarrow CO_2 + C$
-
- Direct oxidation: $C_3H_8 + 10O_O^X \rightarrow 3CO_2 + 4H_2O + 10V_O^{\bullet\bullet} + 20e'$
 - Hydrogen oxidation: $H_2 + O_O^X \rightarrow H_2O + V_O^{\bullet\bullet} + 2e'$
 - CO oxidation: $CO + O_O^X \rightarrow CO_2 + V_O^{\bullet\bullet} + 2e'$

Problems with Practical Fuels

➤ Carbon Deposition

Internal Steam Reforming

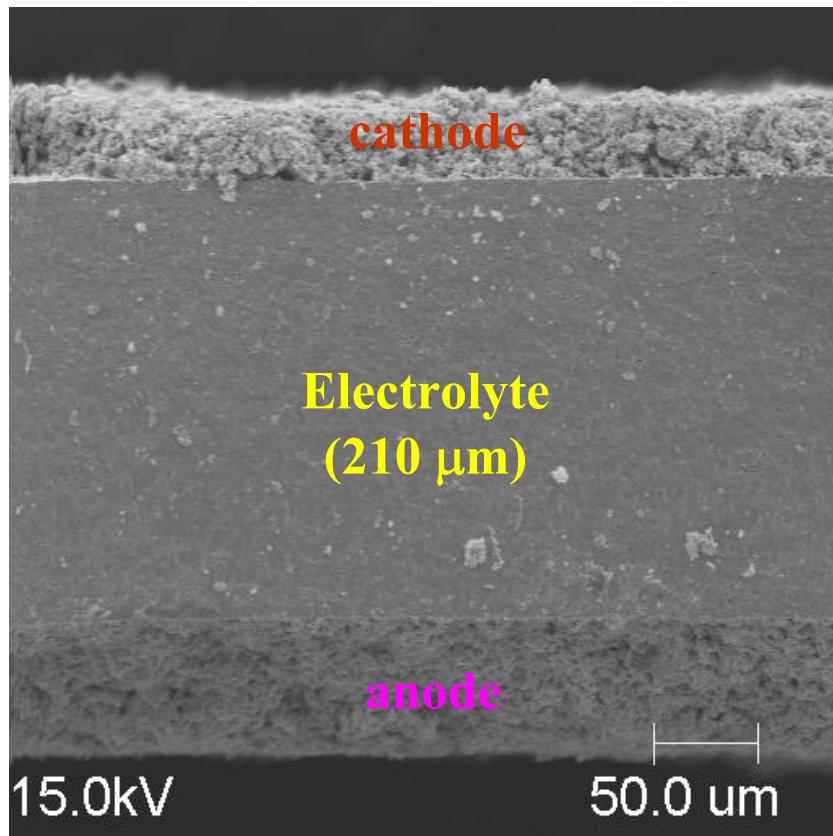
S/C > 2 :1, high cost, low efficiency

➤ Sulfur Poisoning

➤ Active Catalyst at Low Temperatures

Cell Configuration I – Effect of microstructure

Electrolyte–Supported SOFC

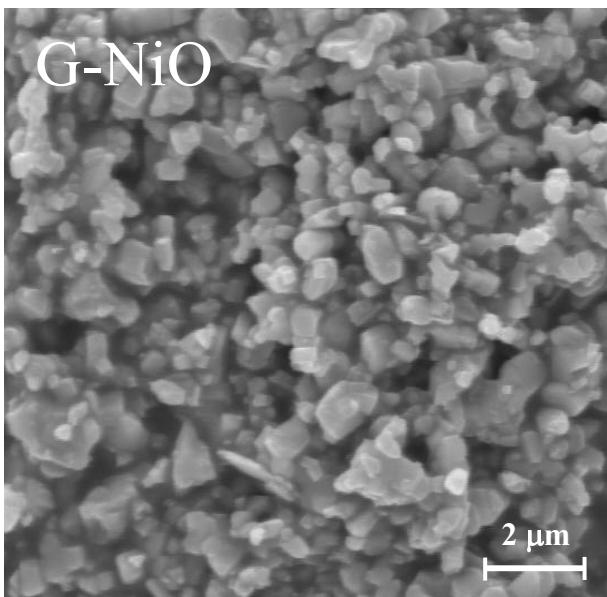
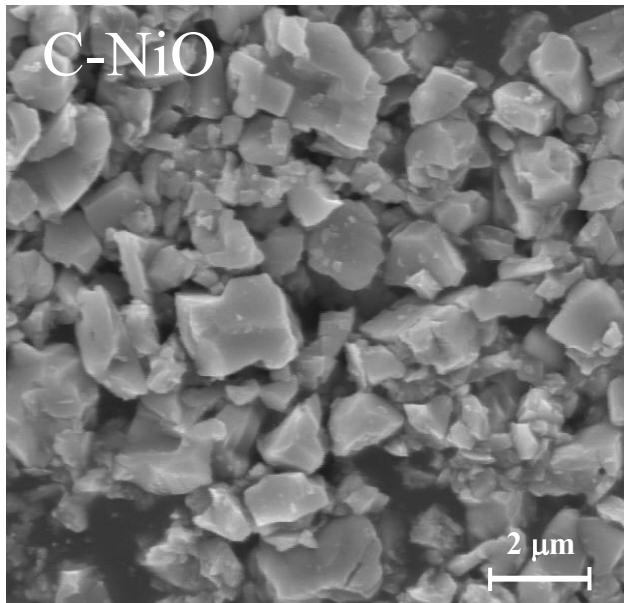


70%SSC-30%GDC
Screen Printing

Die pressing

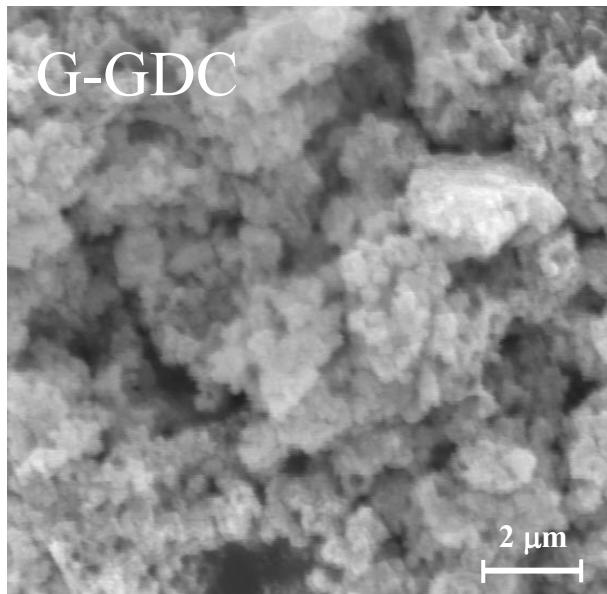
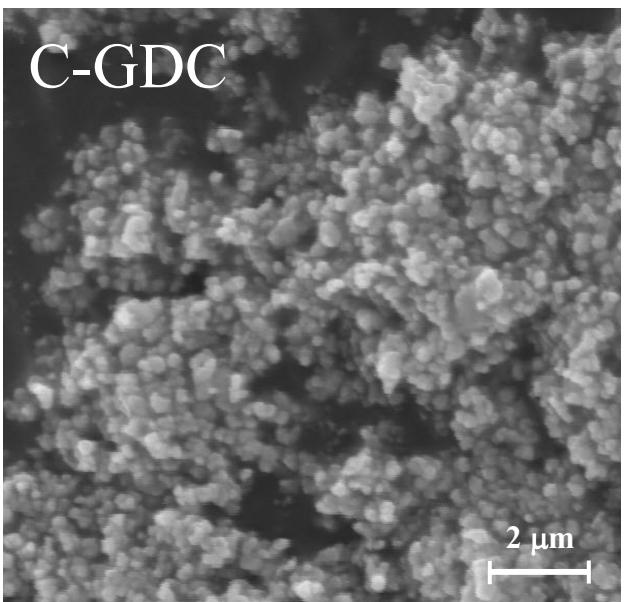
Ni-GDC
dip-coating

Morphology of Precursor Powders



**NiO
Powders**

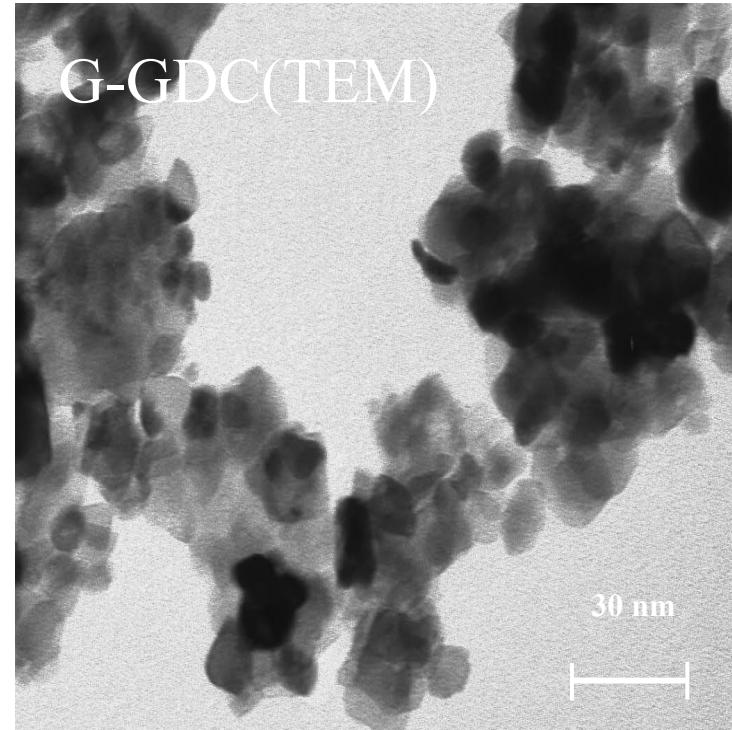
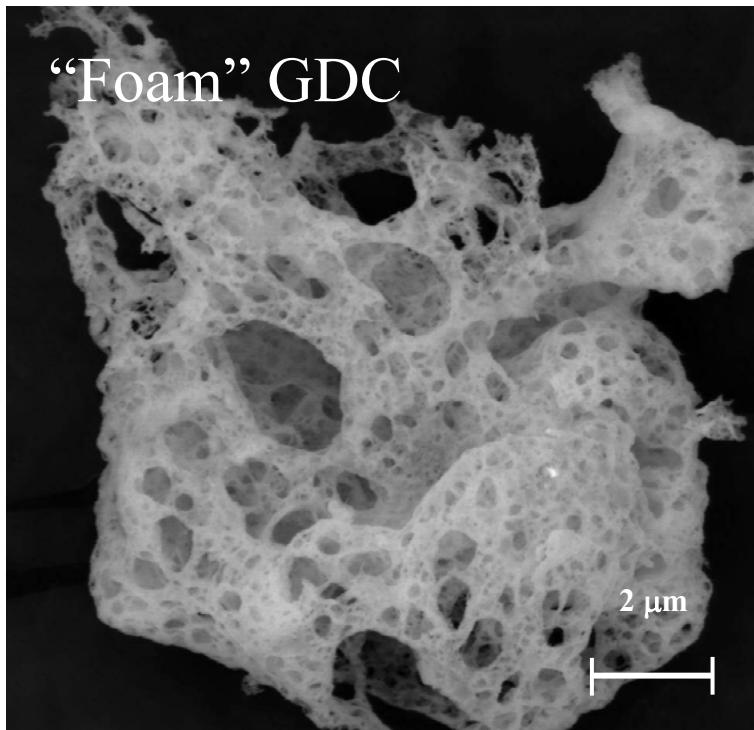
C=Commercial
G=Glycine Nitrate
process



**DCC
Powders**

GT – FC/BT

GDC Powders by GNP



Anode Components

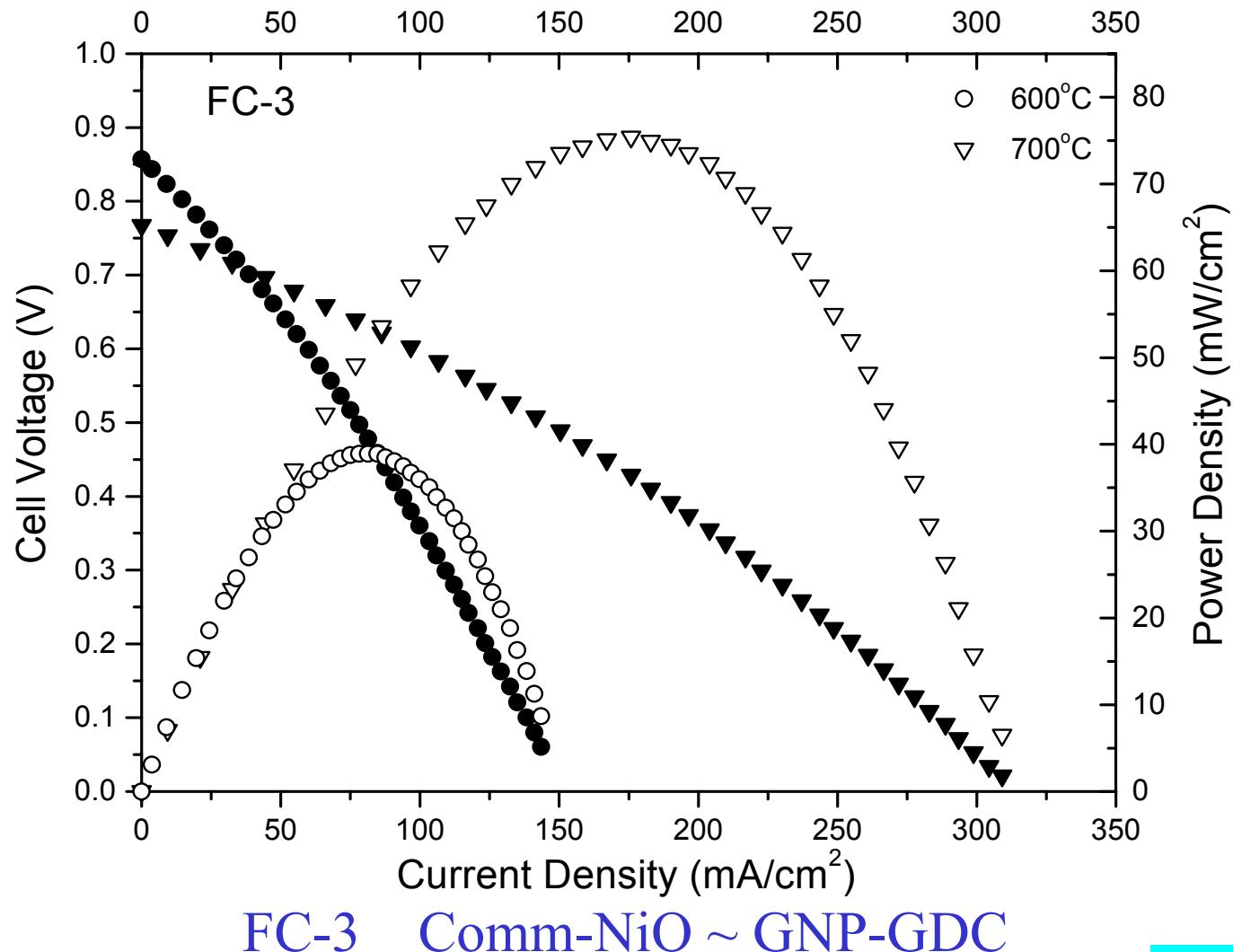
Comm-NiO GNP-NiO Comm-GDC GNP-GDC

2.0 μm 0.8 μm 0.3 μm 0.02 μm

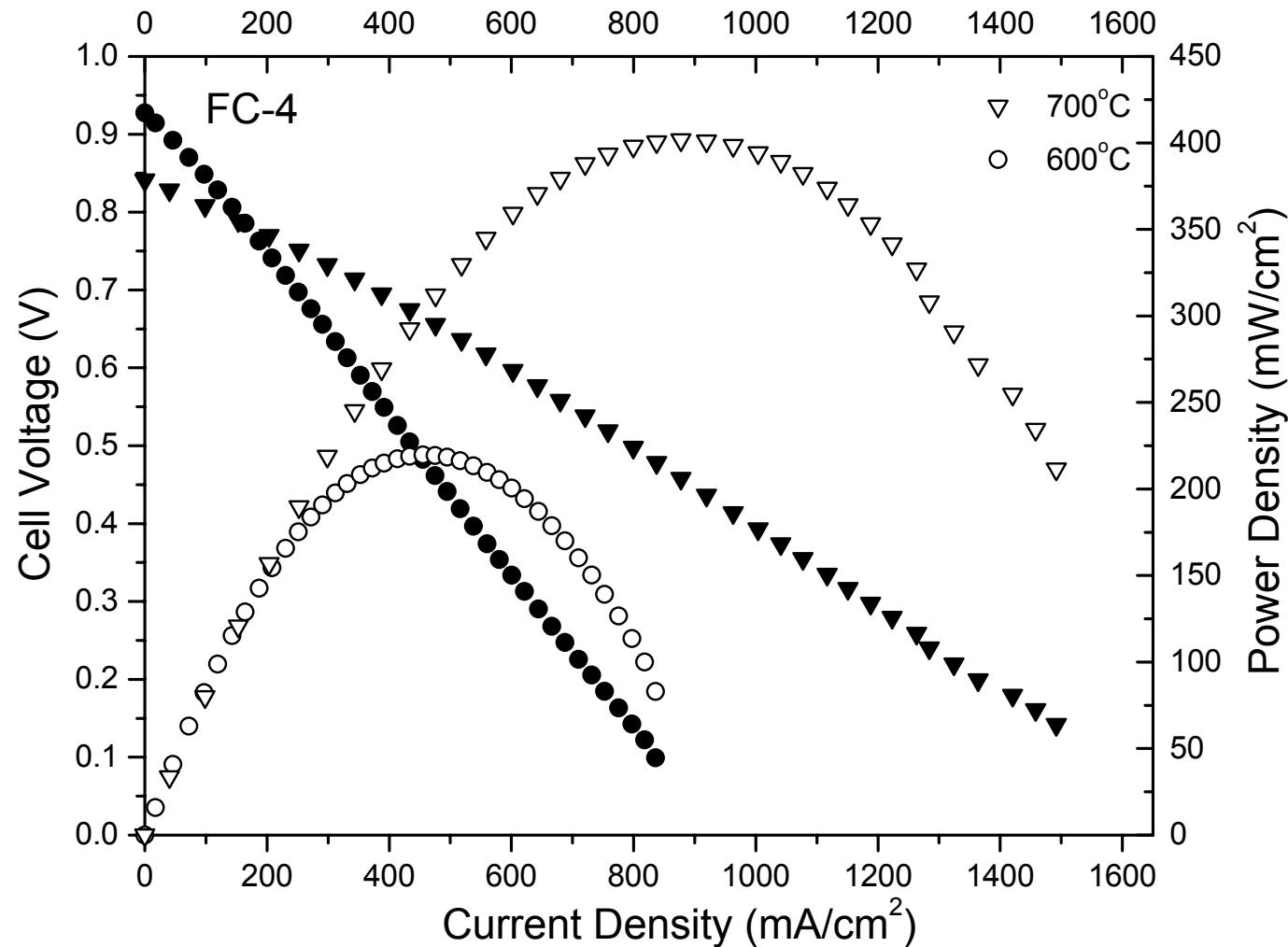


Fuel cell	Anode component	Weight proportion (%)
FC-1	Comm-NiO~Comm-GDC	65: 35
FC-2	GNP-NiO ~ Comm-GDC	65: 35
FC-3	Comm-NiO ~ GNP-GDC	65: 35
FC-4	GNP-NiO ~ GNP-GDC	65: 35

Effect of Microstructure on Performance

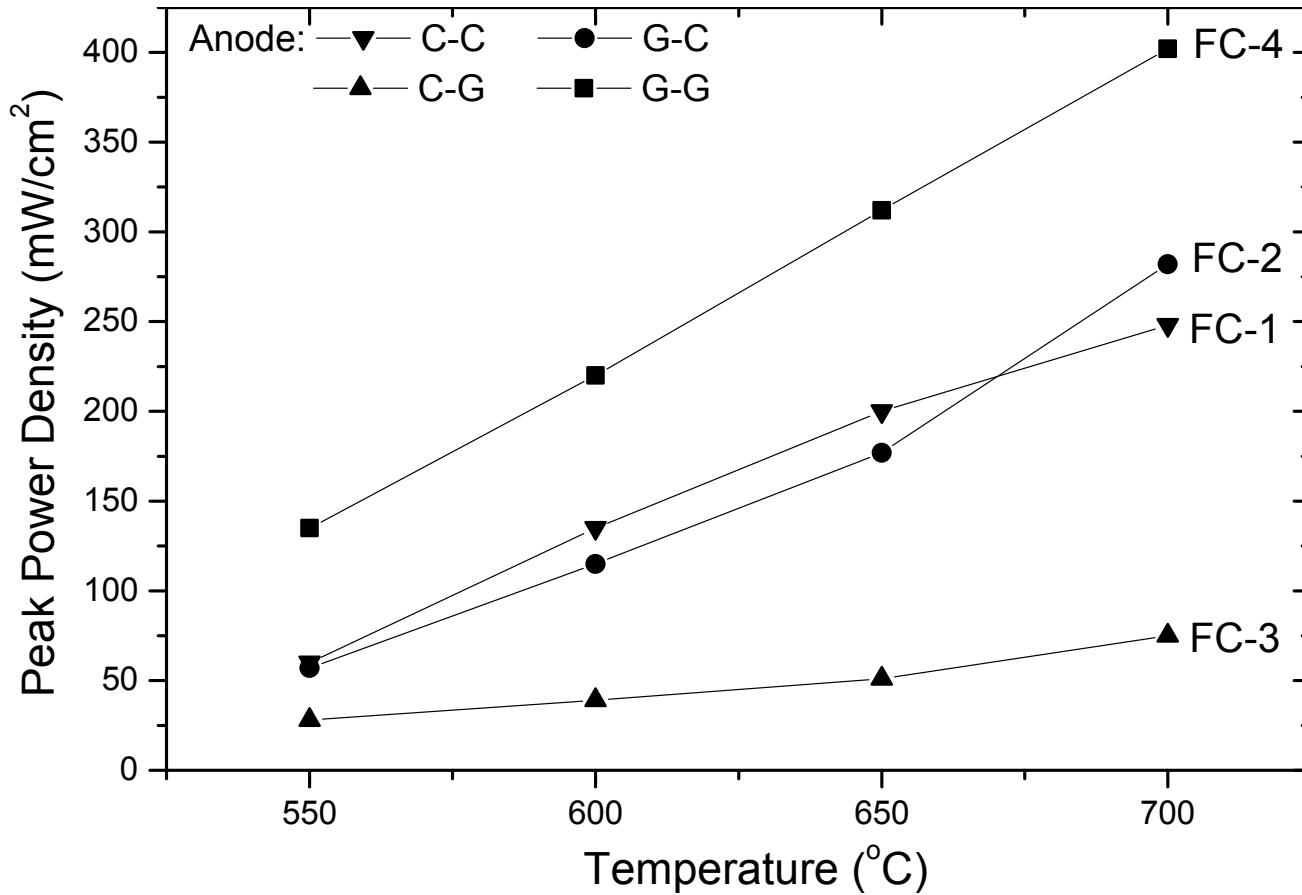


Microstructure on Performance

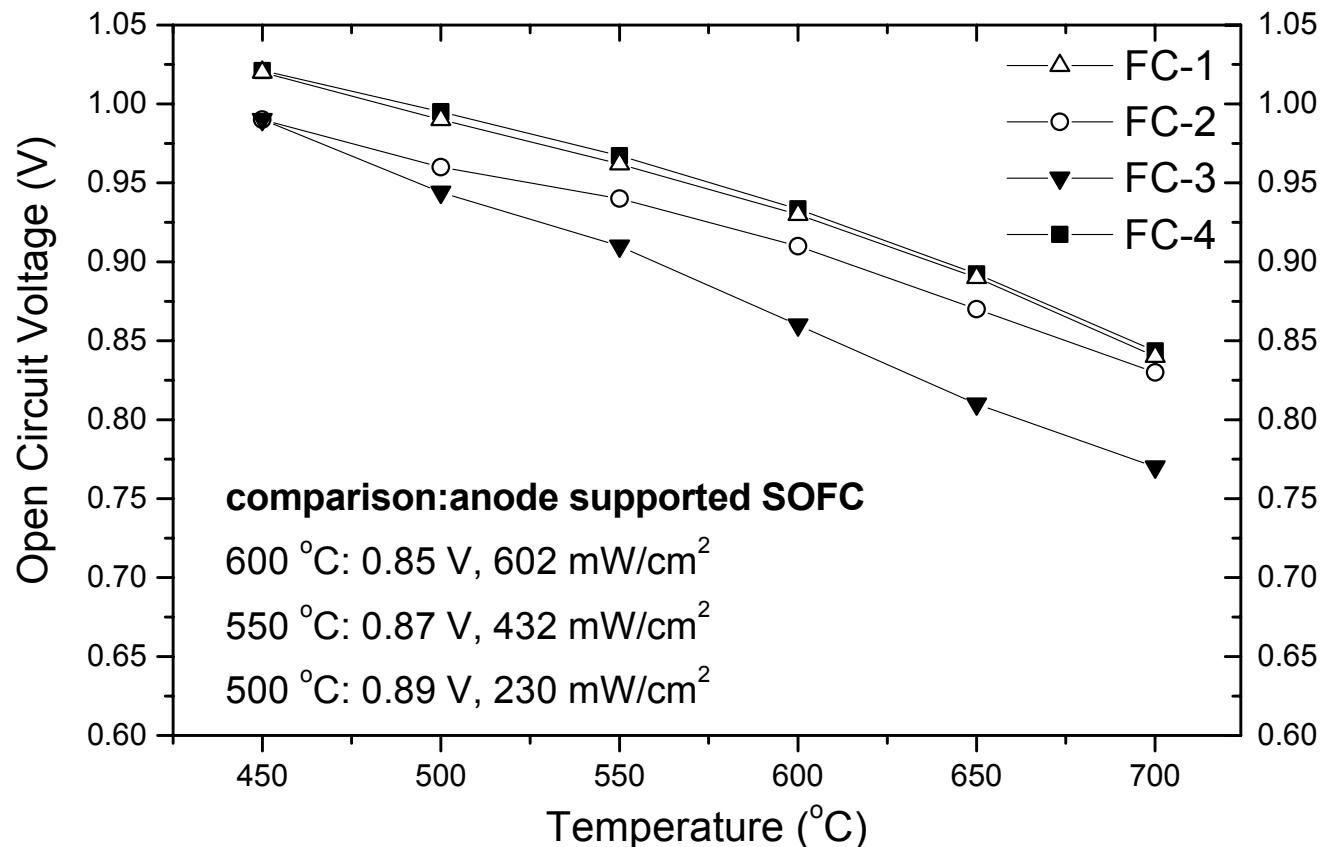


FC-4 GNP-NiO ~ GNP-GDC

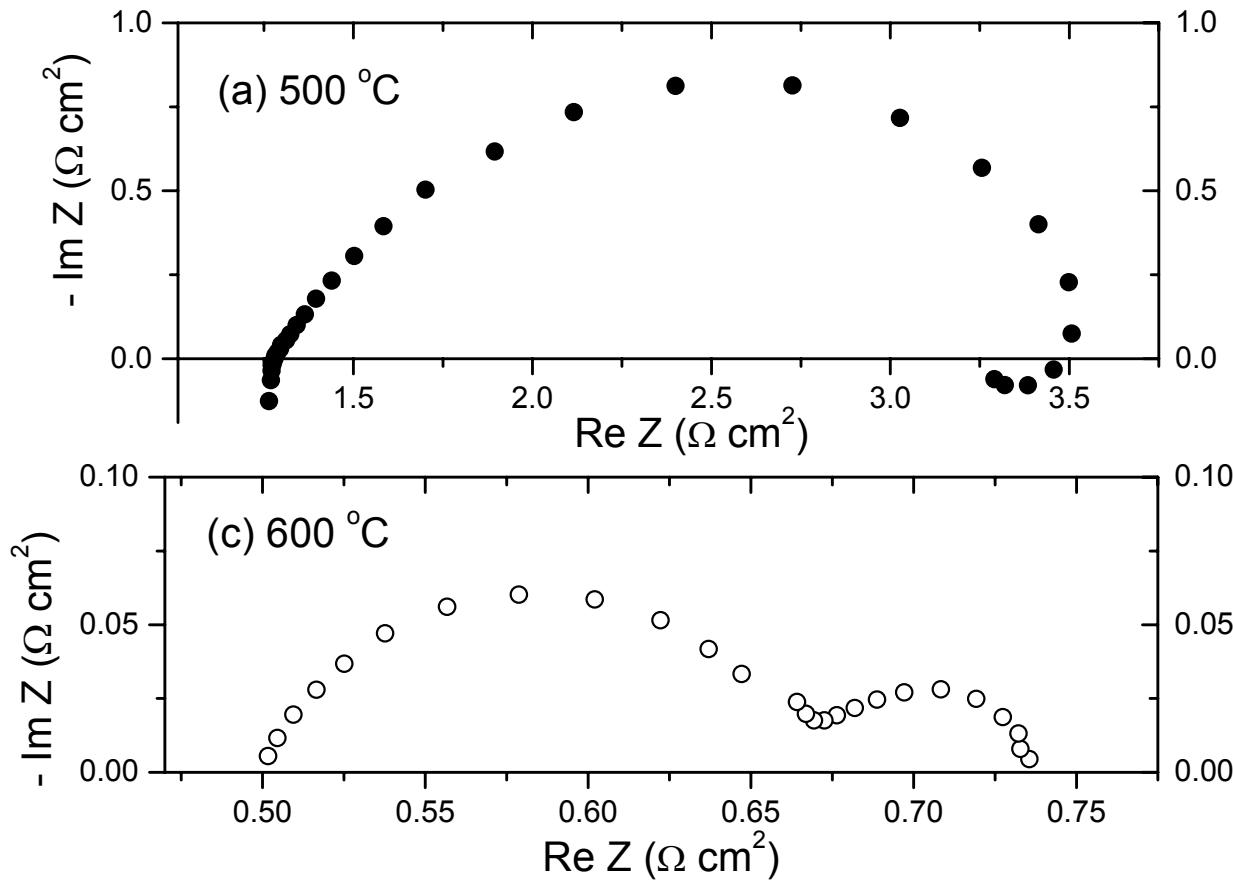
Peak Power Densities



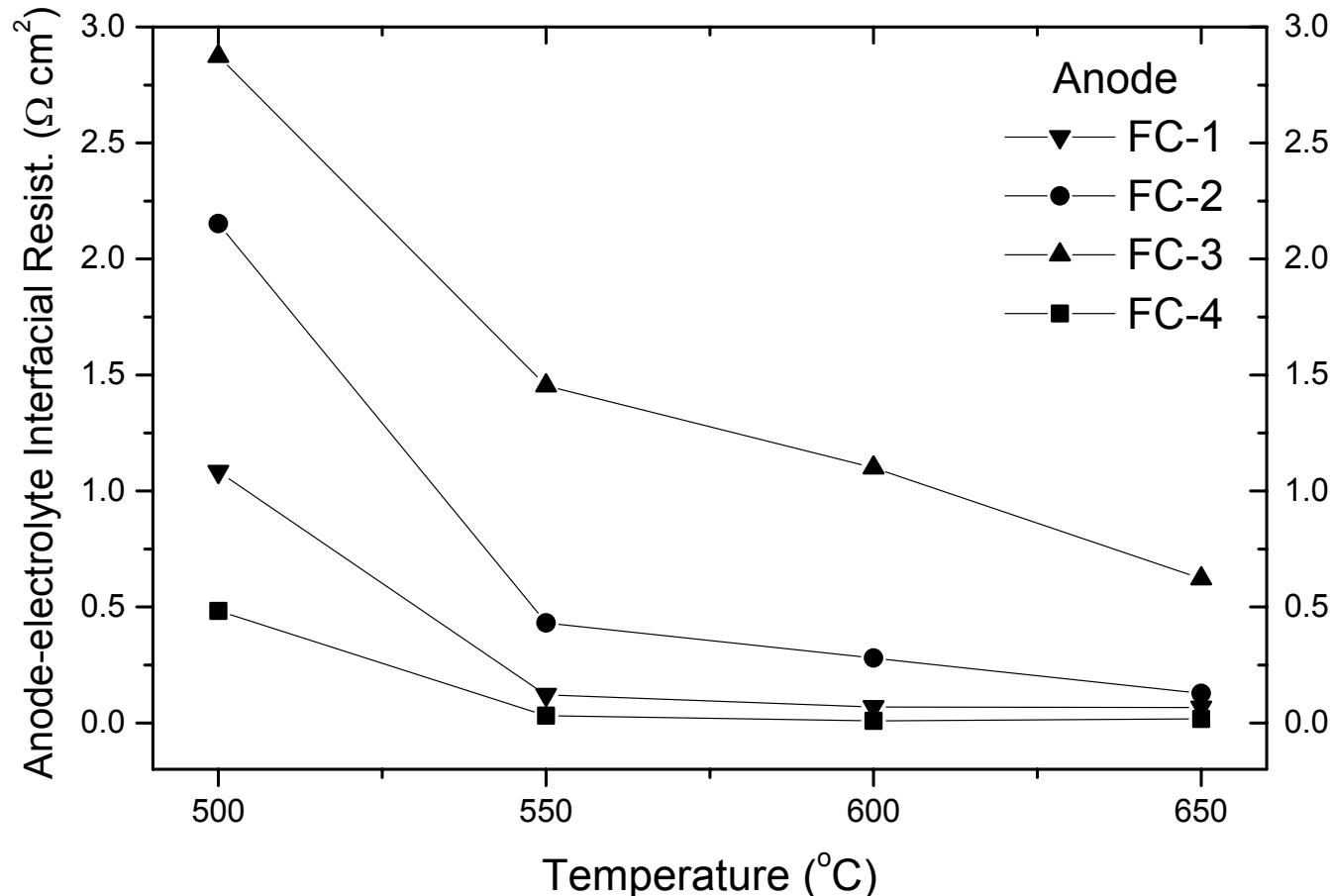
Open Circuit Potentials



Impedance Spectra (FC-4)



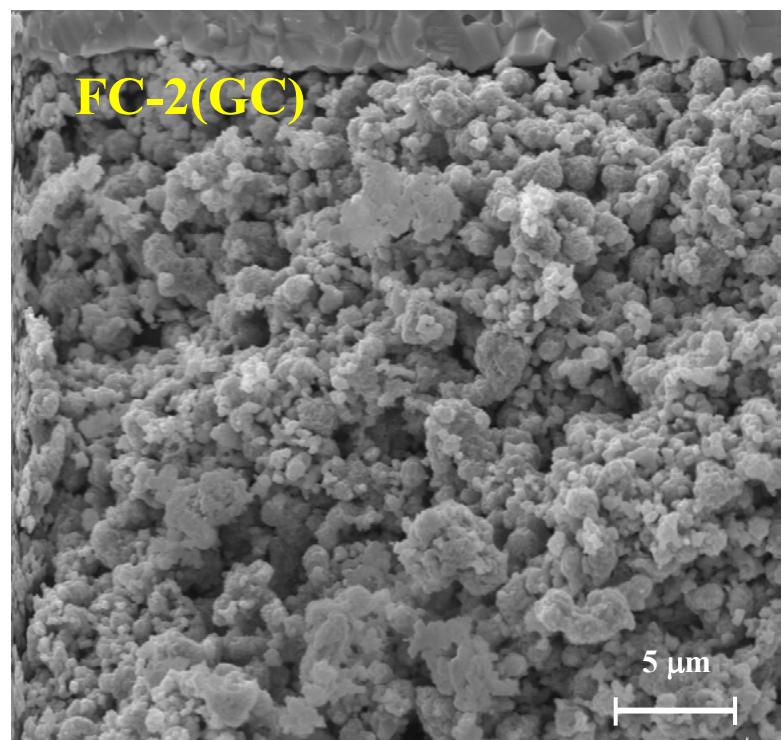
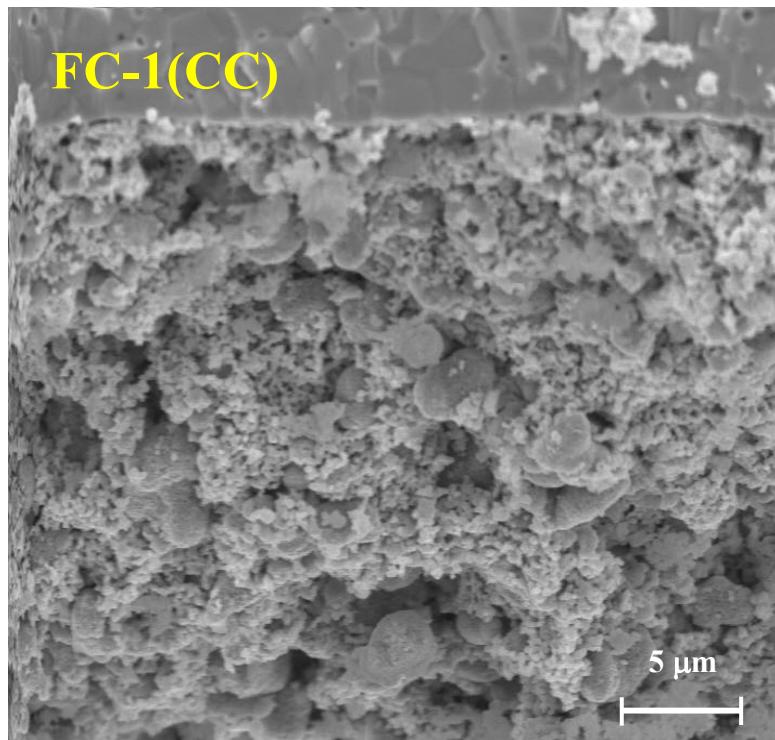
Interfacial resistance between anode and electrolyte



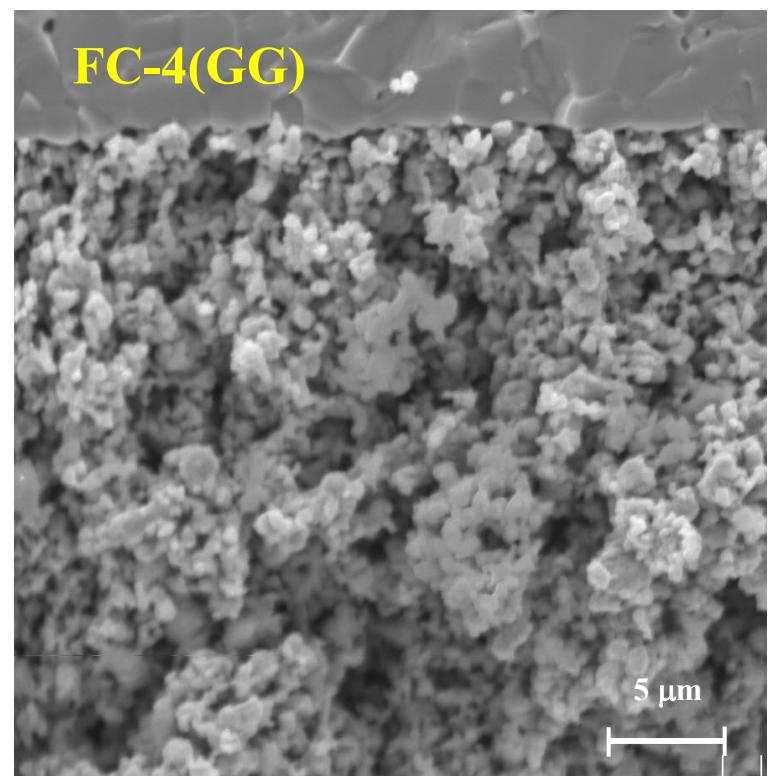
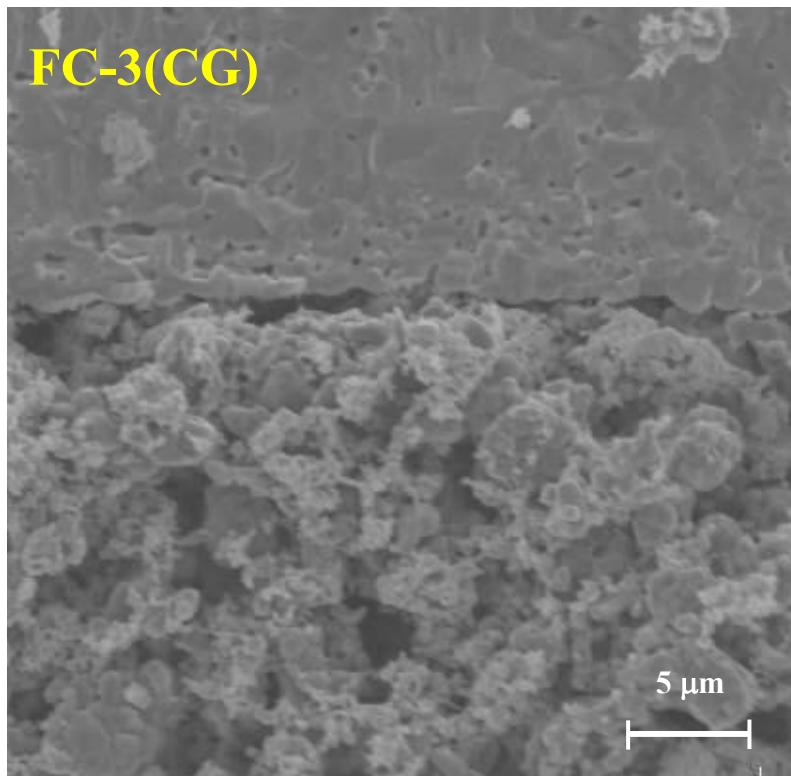
Area specific Ohmic drop, anode/electrolyte interfacial resistance ($\Omega \text{ cm}^2$) at 600 °C

	FC-1(CC)	FC-2(GC)	FC-3(CG)	FC-4(GG)
Total	1.22	1.12	3.59	0.73
Ohmic Drop	0.93	0.39	2.29	0.50
R_{a+c}	0.29	0.53	1.30	0.23
R_a	0.07	0.31	1.08	0.01

Anode Microstructure

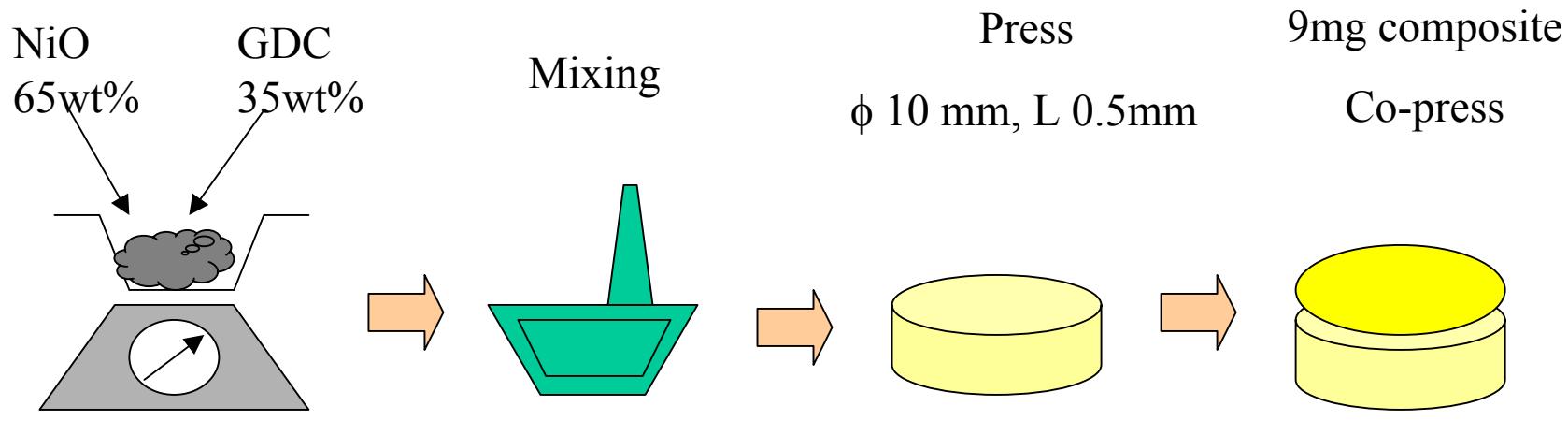


Anode Microstructure



Cell Configuration II – Type of fuels

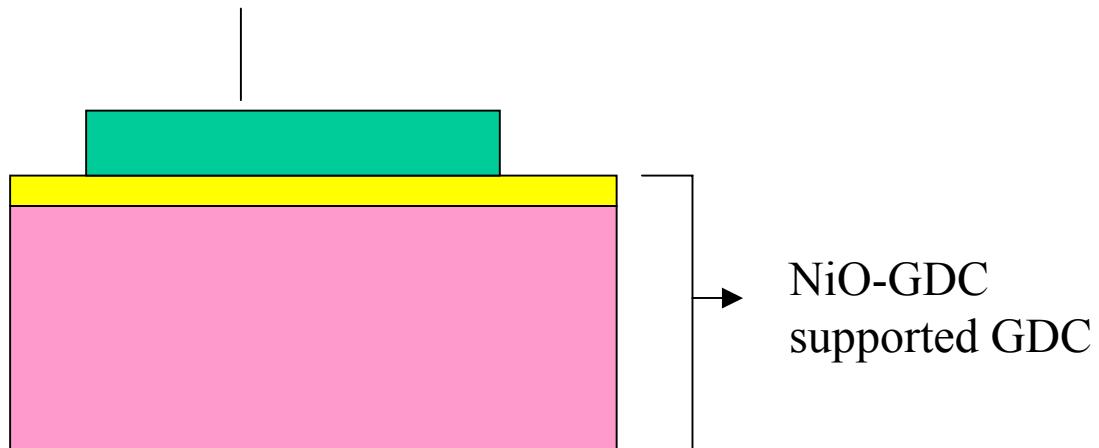
Anode-Supported Electrolyte (Ni-Based Anodes)



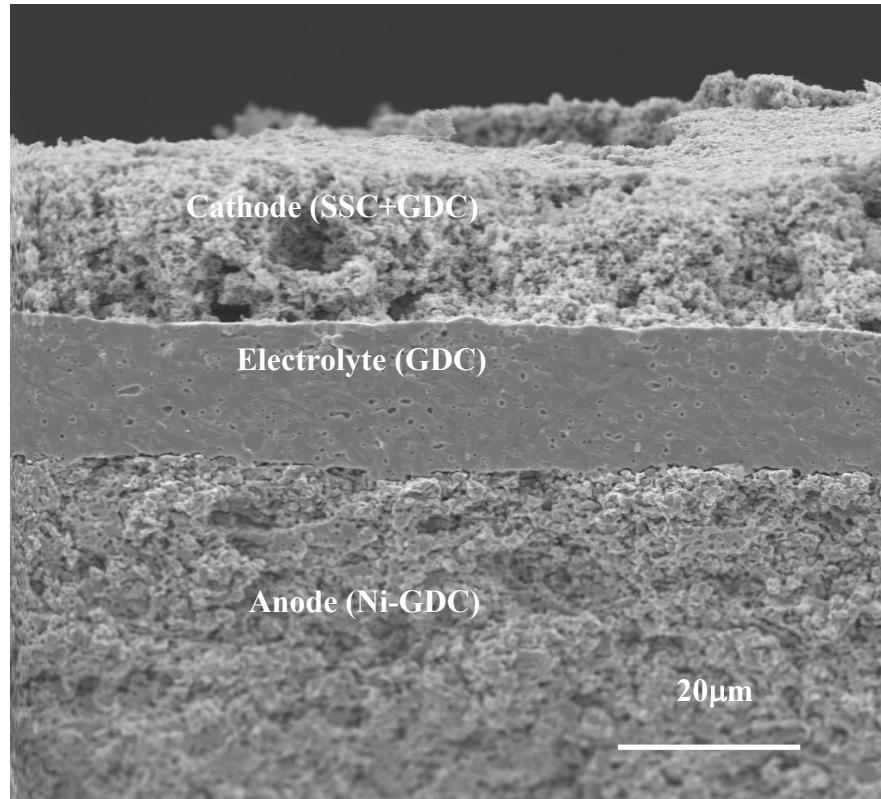
Fired @ 1350 °C/5h
NiO-GDC/GDC

Application of Cathode

Cathode: SSC-GDC
Screen-printing

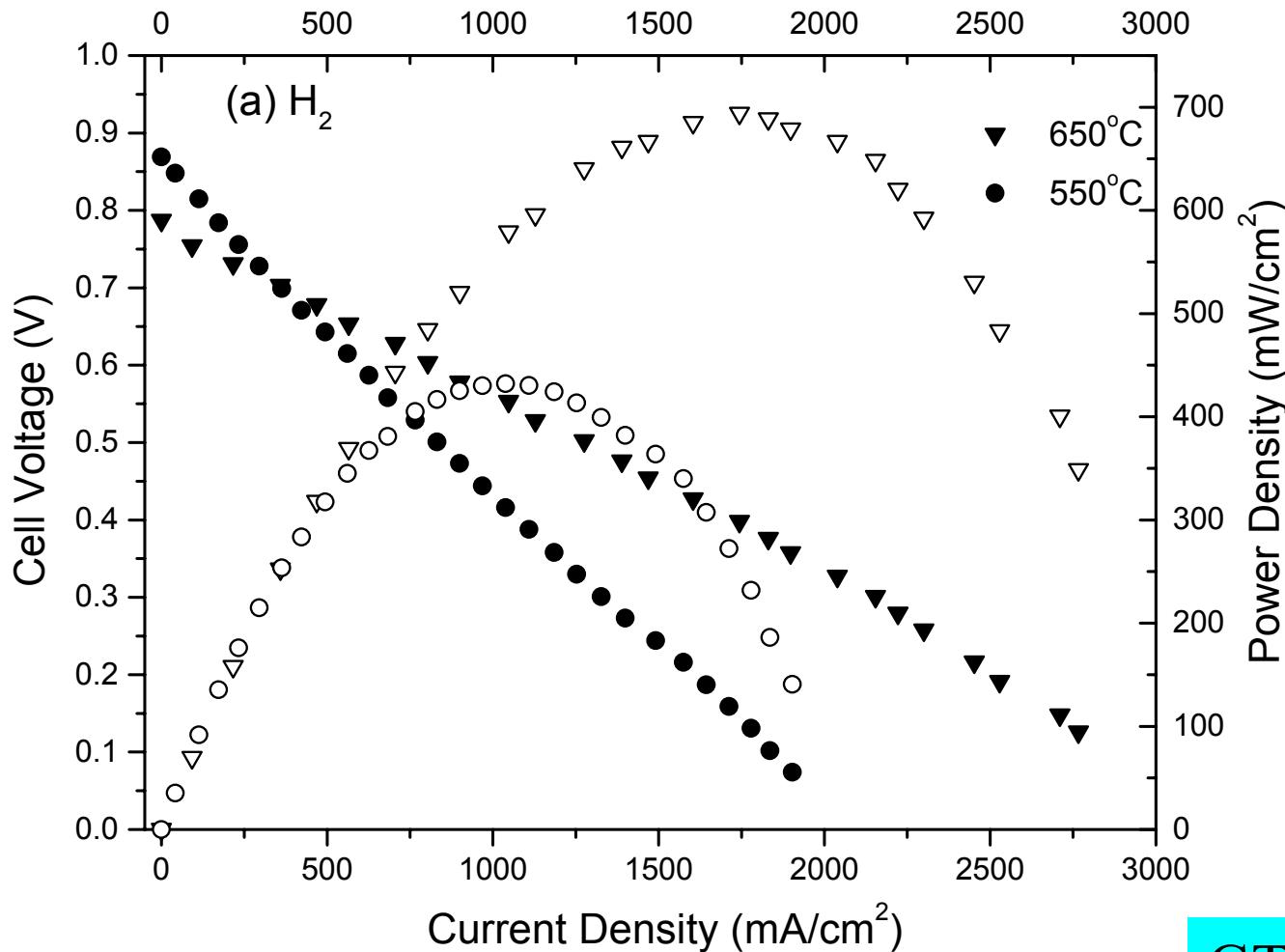


Cross-Sectional View of NiO/GDC-Supported SOFC

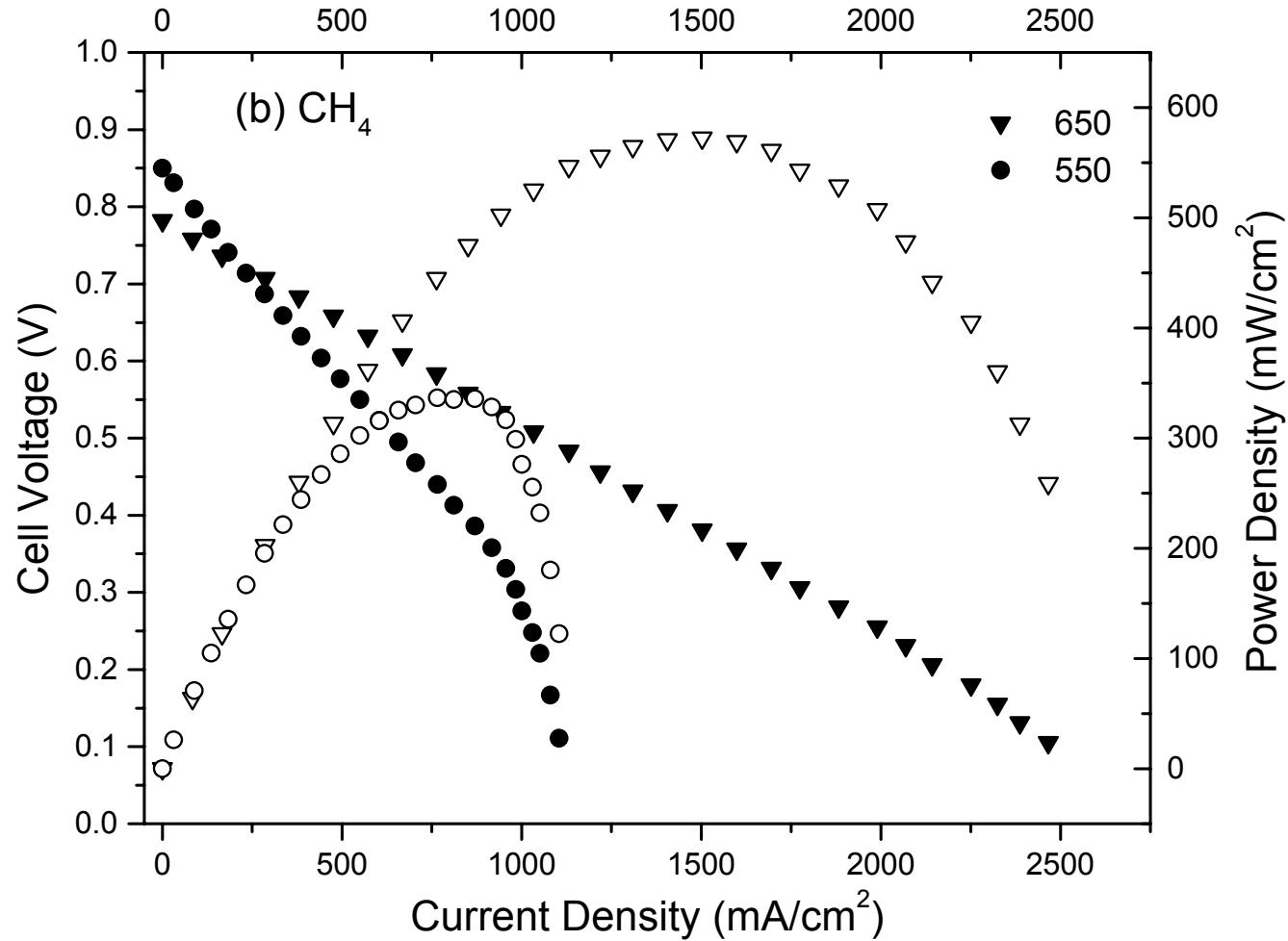


Dependence of Performance on Types of Fuels

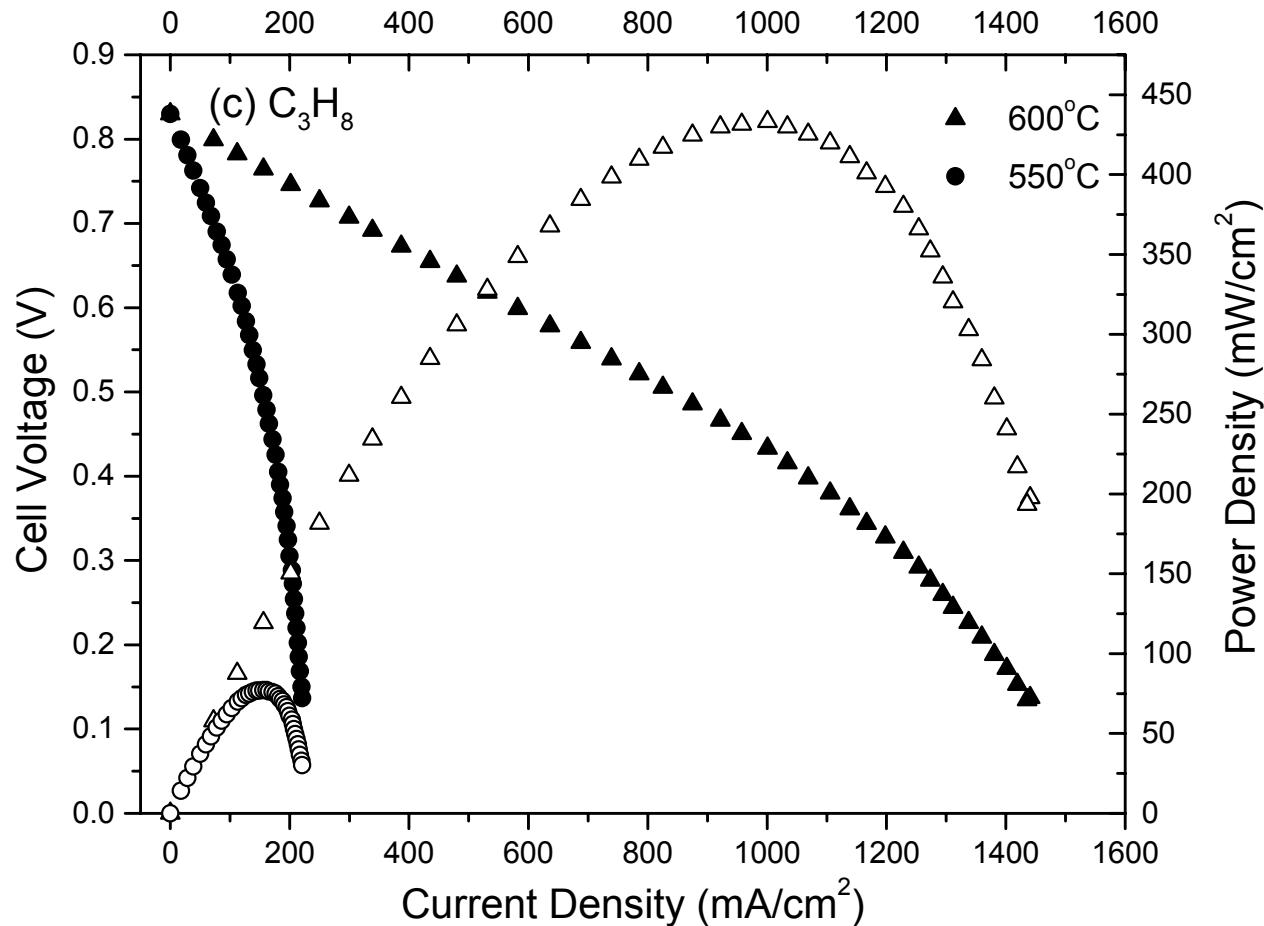
Fuel: H₂



Fuel: Methane



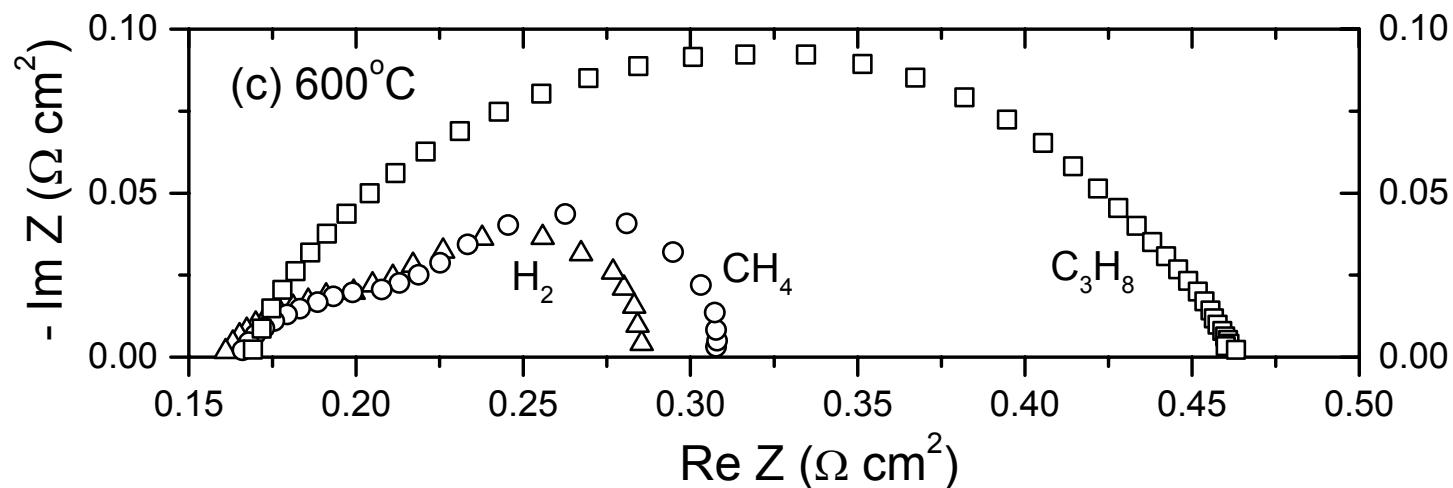
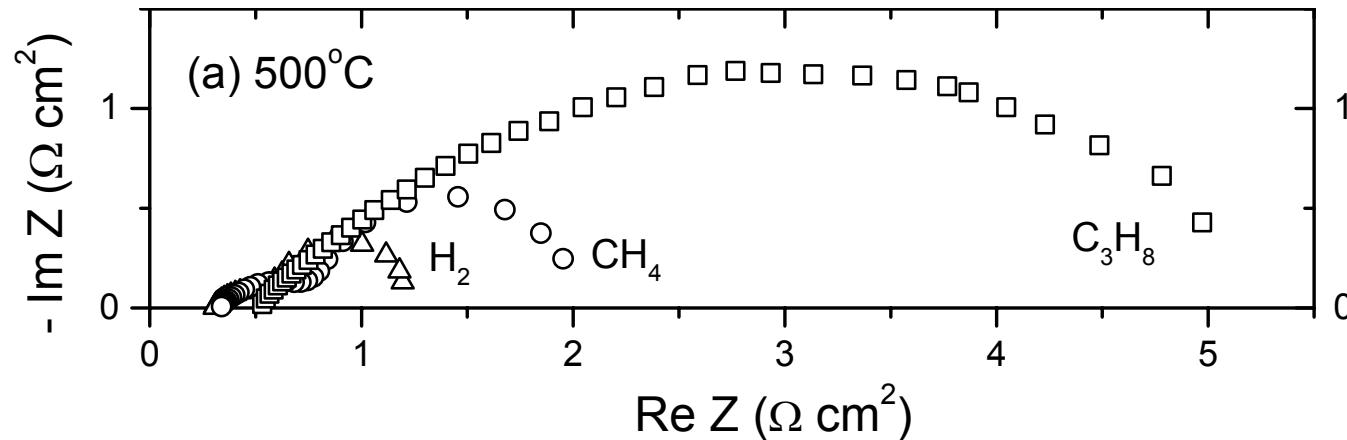
Fuel: Propane



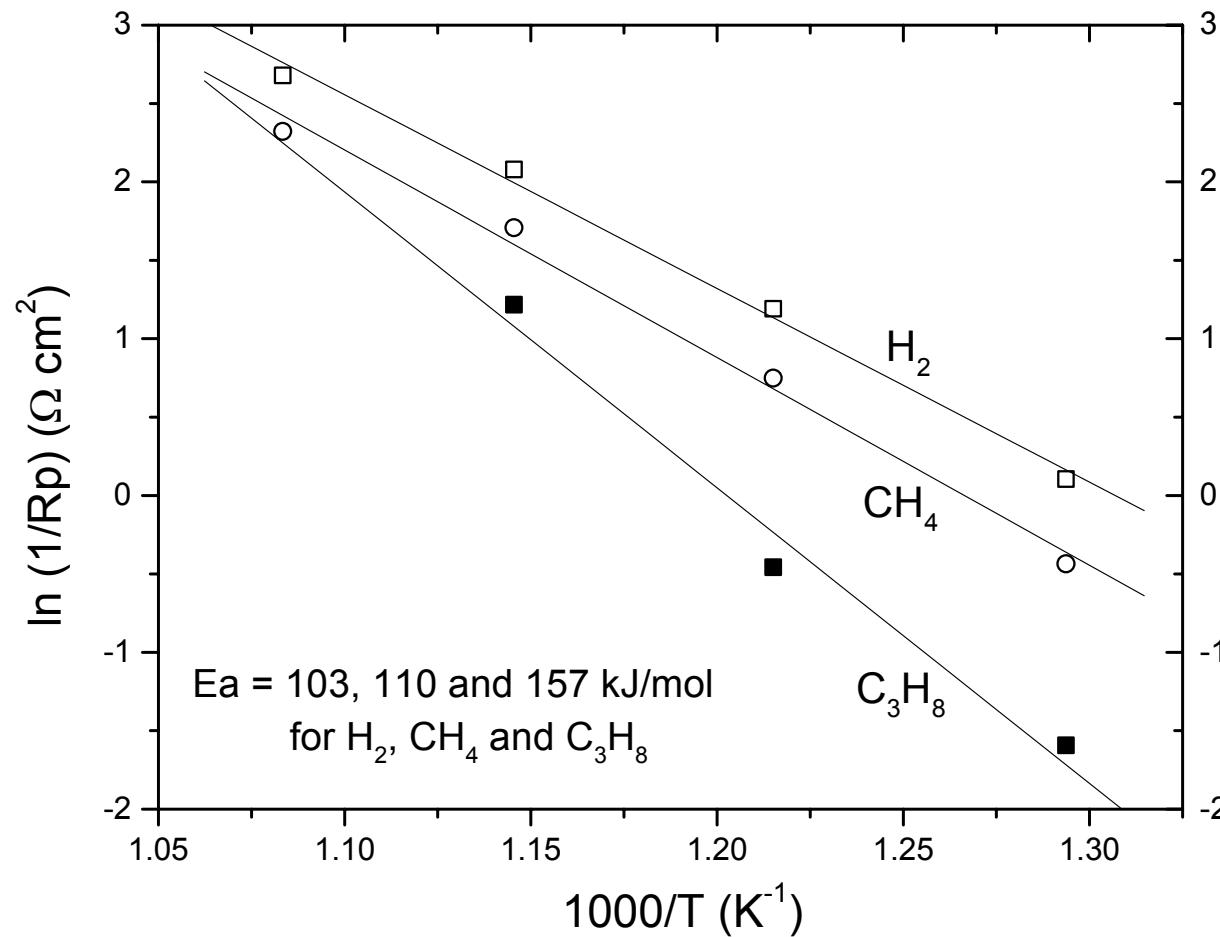
Comparison: H₂, CH₄, C₃H₈

<i>Temp.</i>	<i>fuel</i>	<i>ocv(V)</i>	<i>P_{max}(mW/cm²)</i>
500	H ₂	0.889	230
	CH ₄	0.872	169
	C ₃ H ₈	0.791	27
550	H ₂	0.869	432
	CH ₄	0.850	336
	C ₃ H ₈	0.830	77
600	H ₂	0.852	602
	CH ₄	0.846	519
	C ₃ H ₈	0.830	433

Impedance spectra



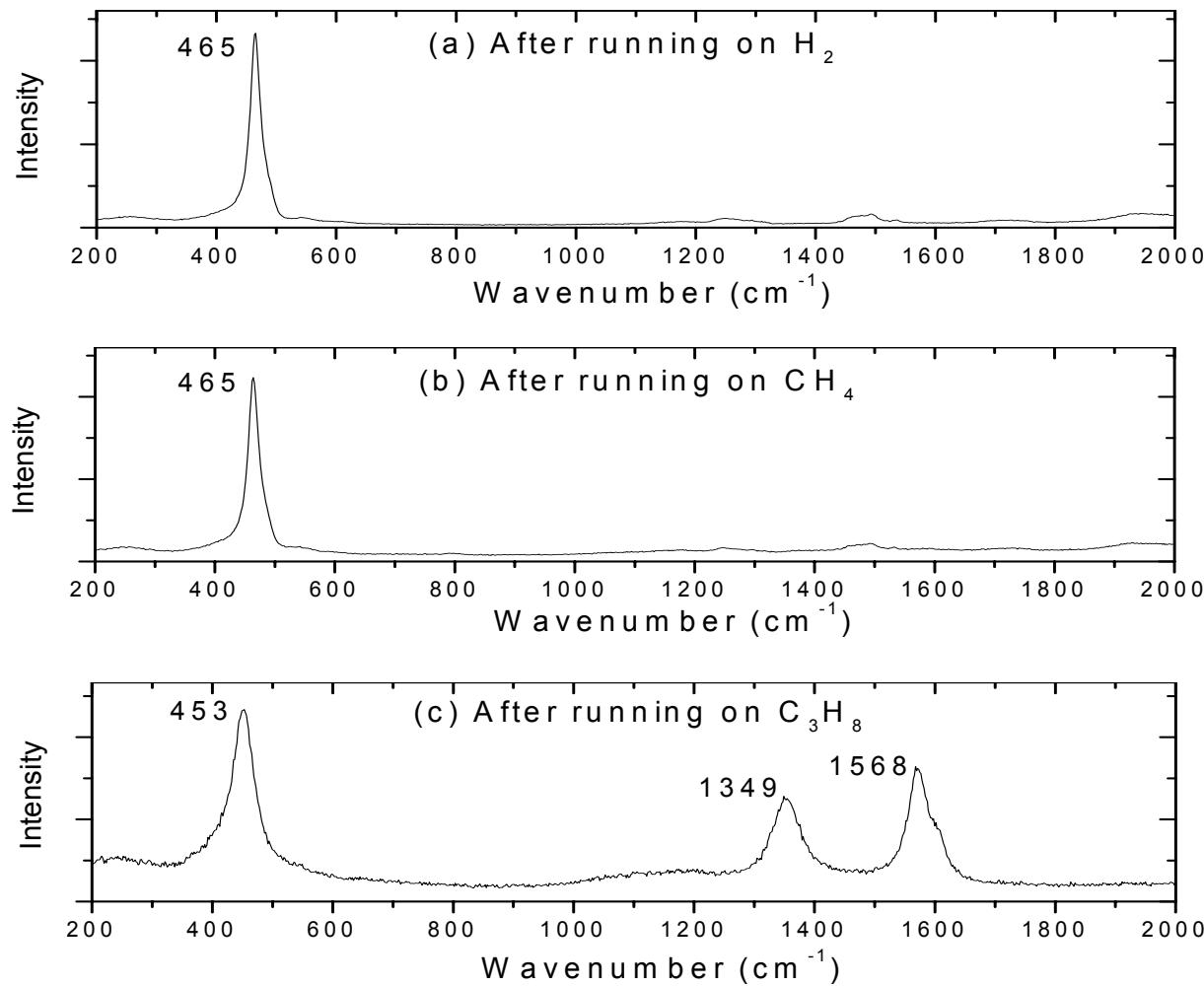
Arrhenius plots of interfacial resistances



Ni-GDC anodes running on
(a) CH_4 for 50 h, and (b) C_3H_8 for 3 h at 600 °C

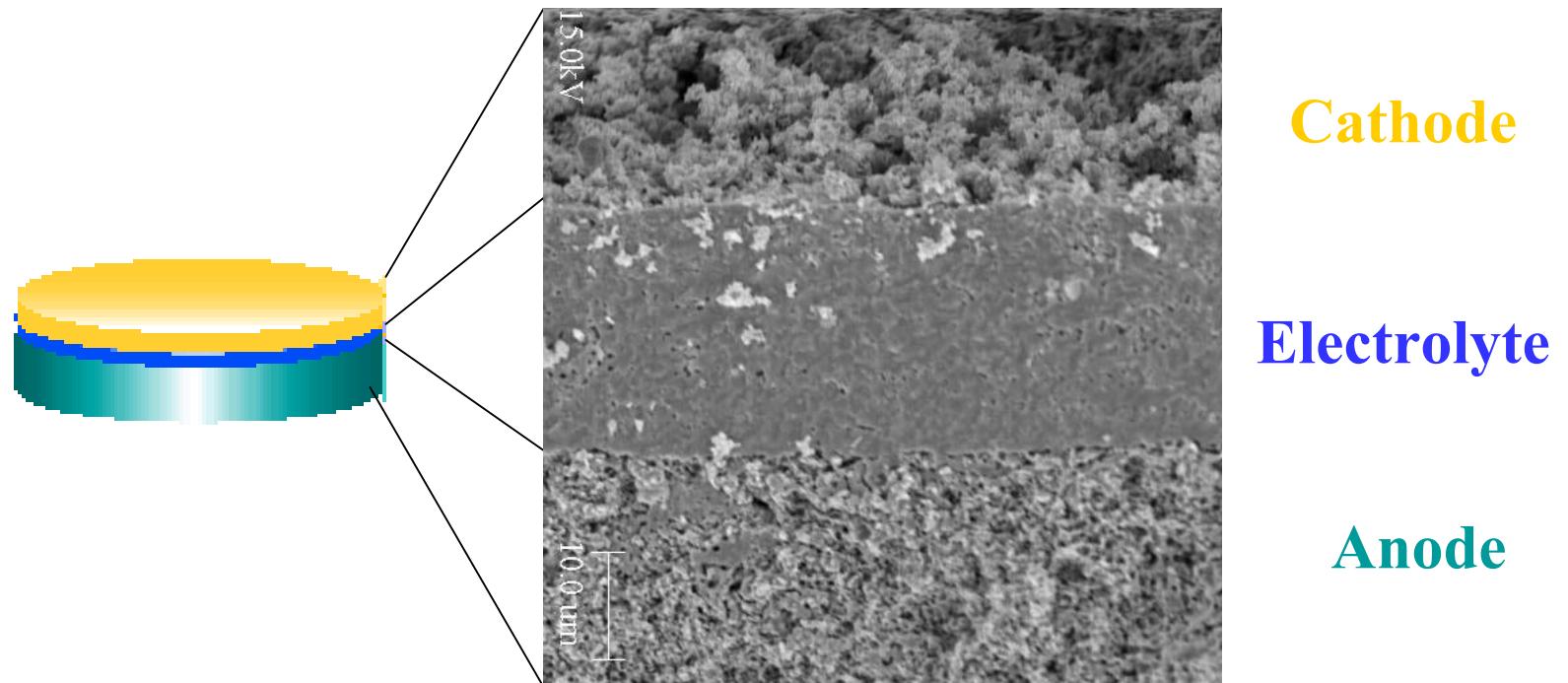


Raman spectra of Ni-GDC surfaces running on H₂, CH₄ and C₃H₈ for 140, 50 and 3 h @ 600 °C



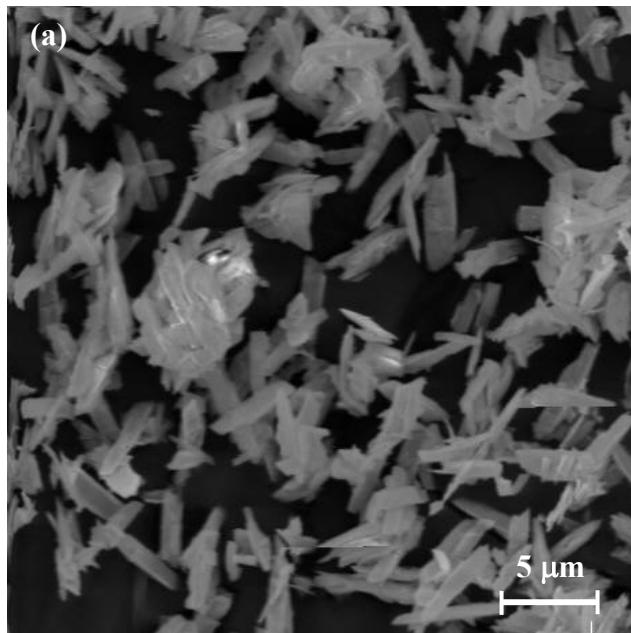
Cell Configuration III

Cu/GDC- Supported SOFC by Co-Pressing and Solution Impregnation

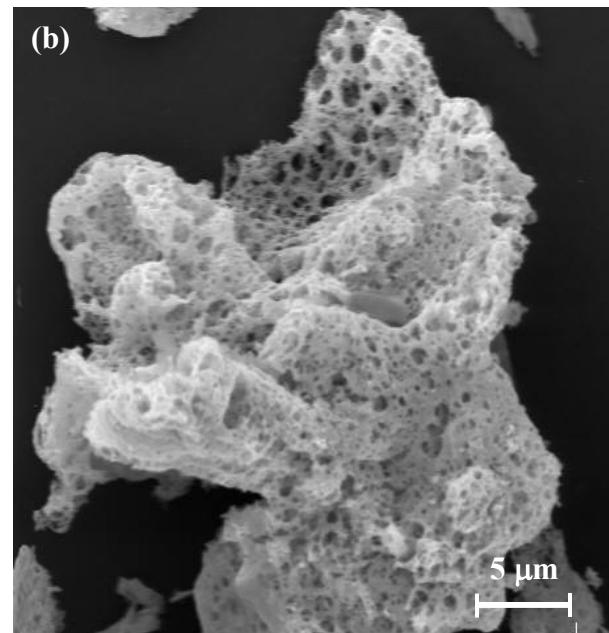


GDC for porous matrix & dense film

For Anode Matrix



For Dense Film



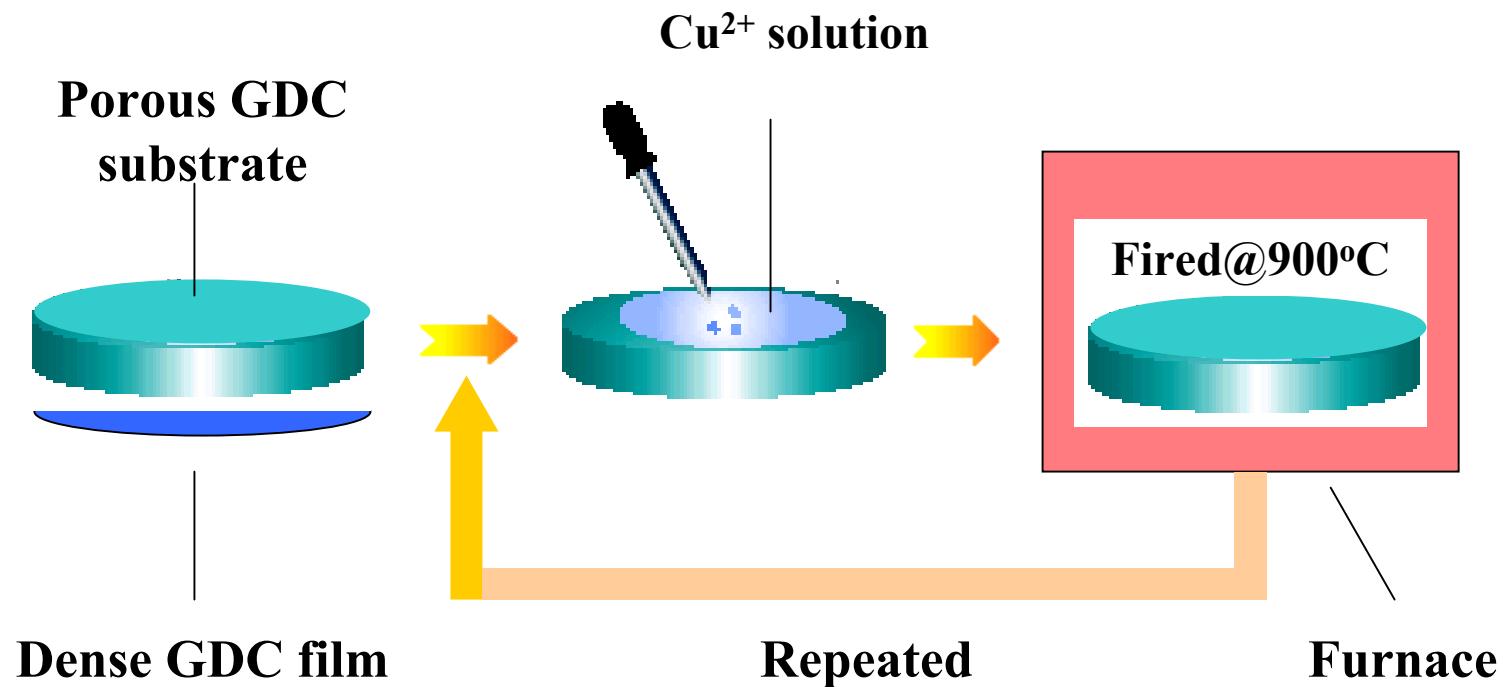
Oxalate coprecipitation

Firing @ $700^\circ\text{C}/1\text{h}$

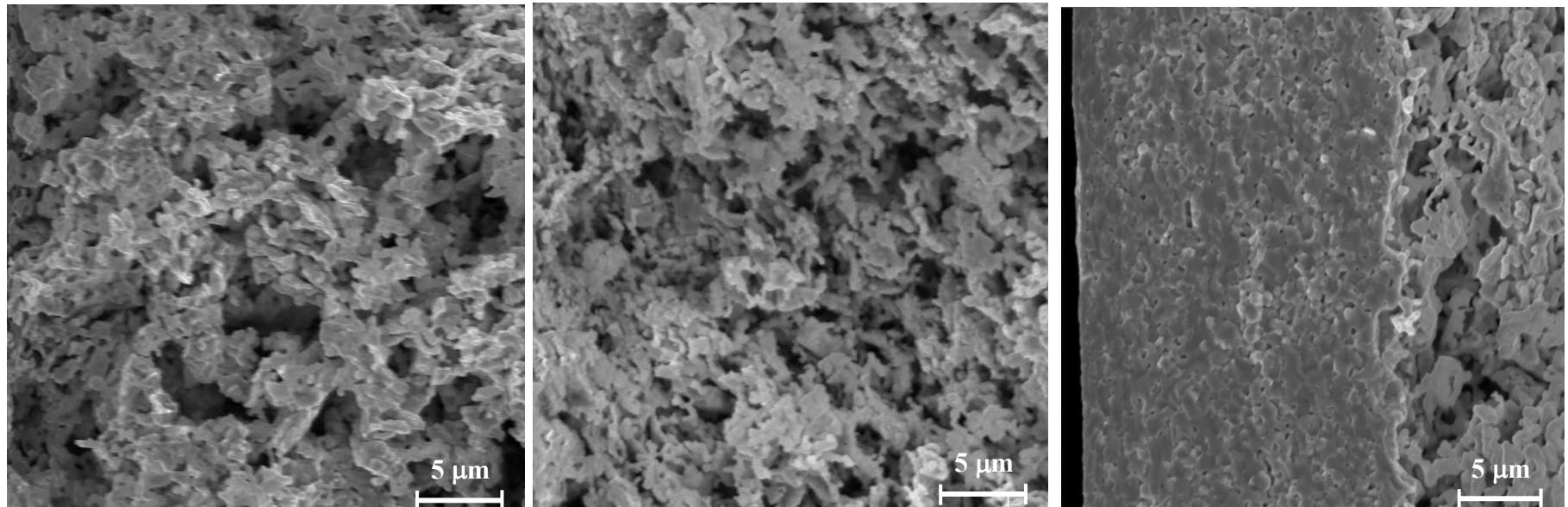
Glycine/nitrate Process

@ $600^\circ\text{C}/2\text{h}$

Fabrication of the Bi-Layer



Anode microstructure



Before
impregnation

After
impregnation

CuO-GDC/GDC

Single fuel cell parameters

Diameter: 0.8cm, Thickness: 0.75mm

Anode matrix density: 2.49g/cm³

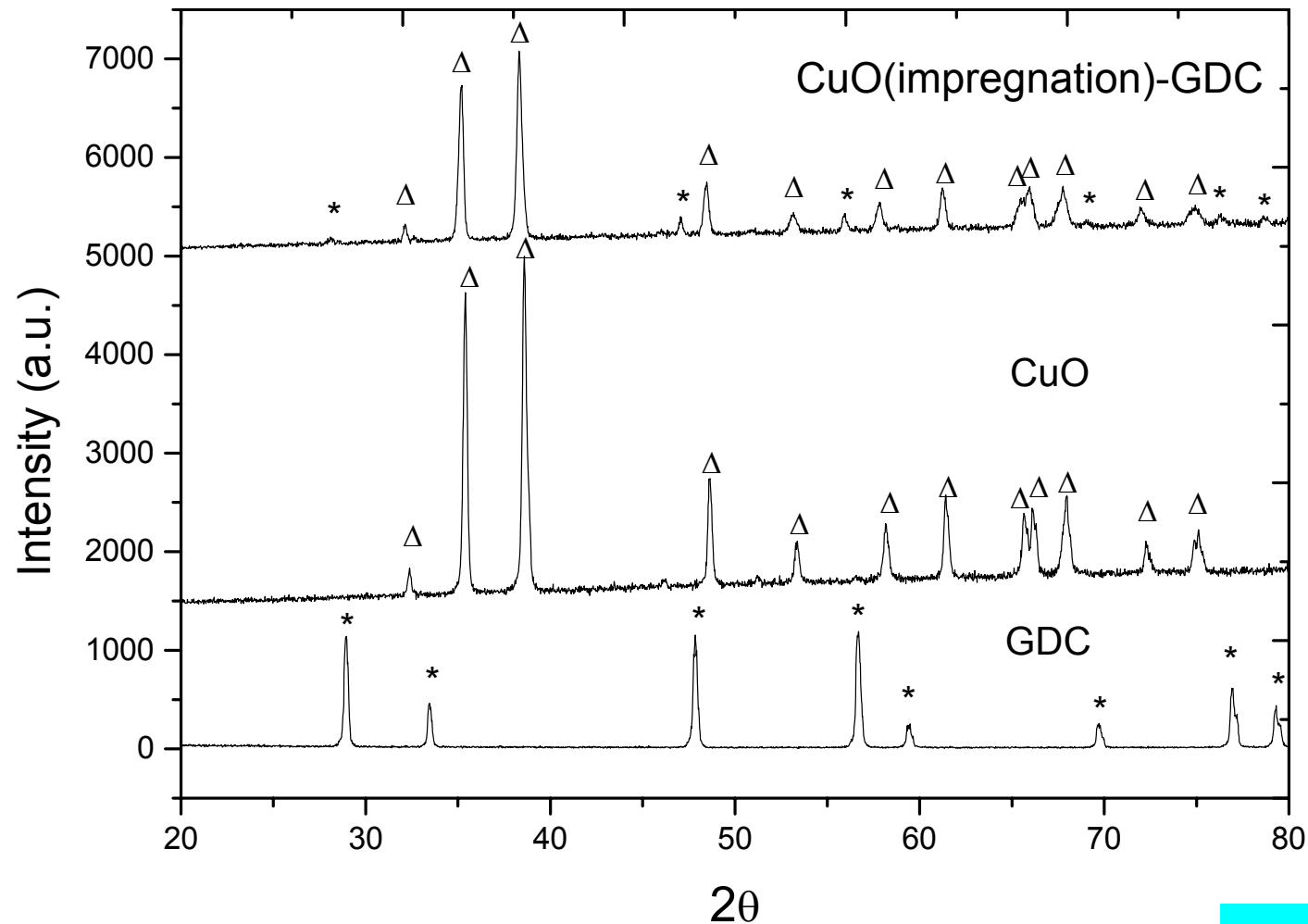
Green porosity before impregnation: 65.7%

GDC volume in anode matrix: 34.3%

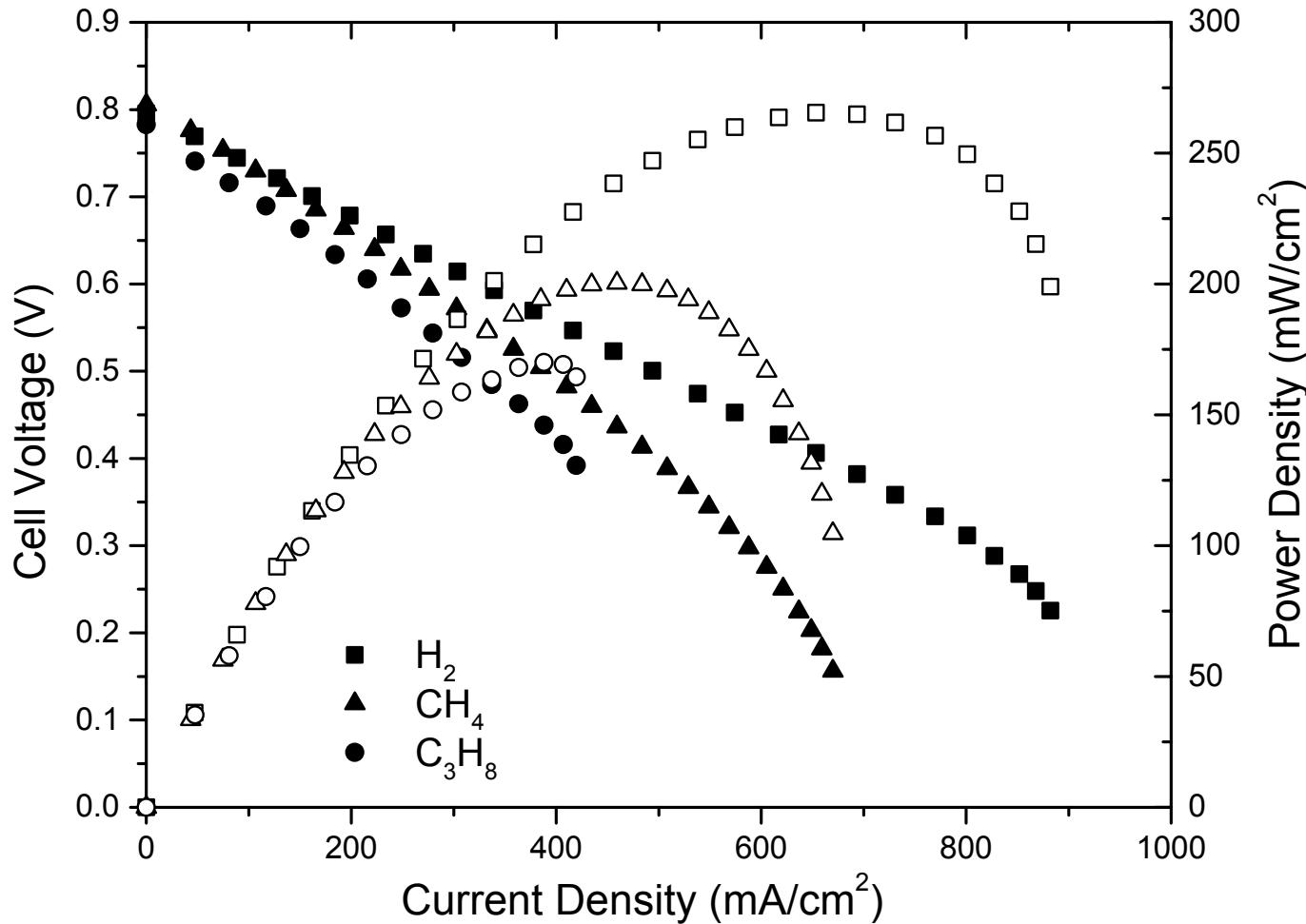
Cu volume percent: 19.8%

Anode porosity after reduction: 45.9%

Cu-GDC Anode-Supported FC (solution impregnation)



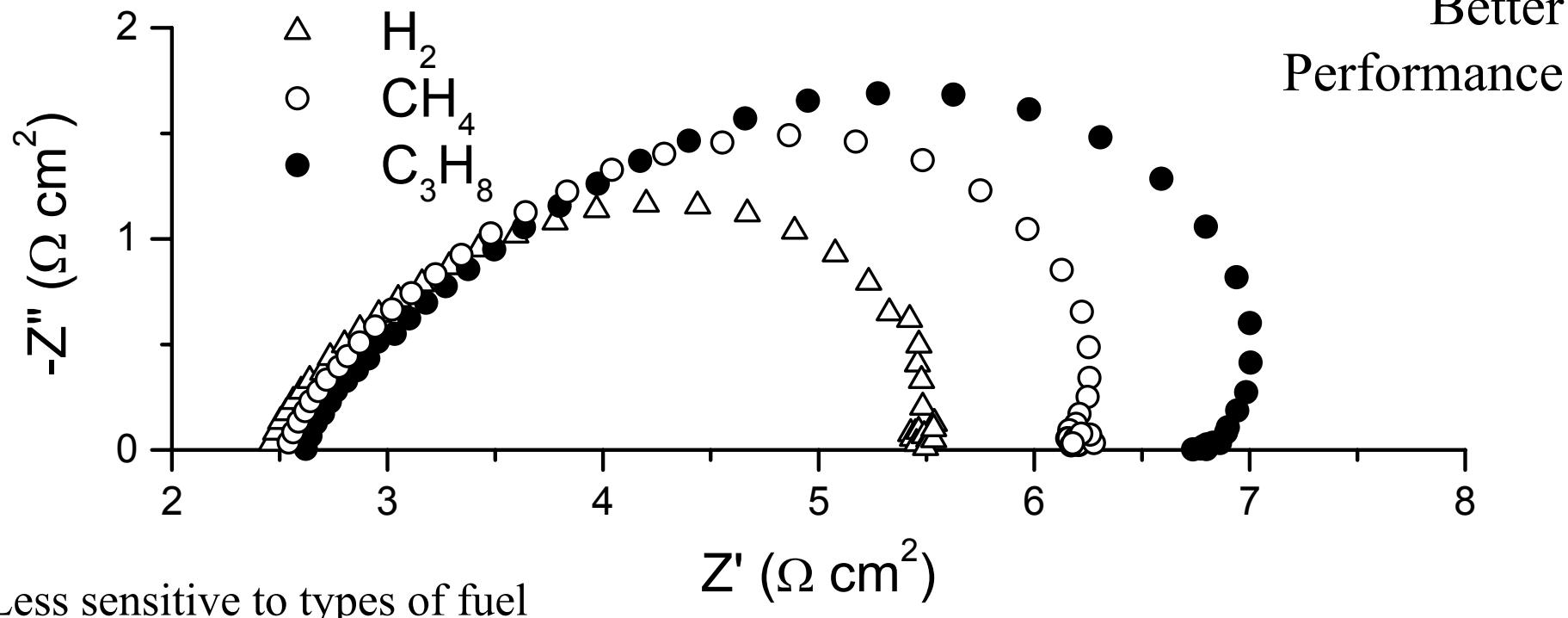
Fuel cell performance Cu-GDC based SOFCs at 600°C



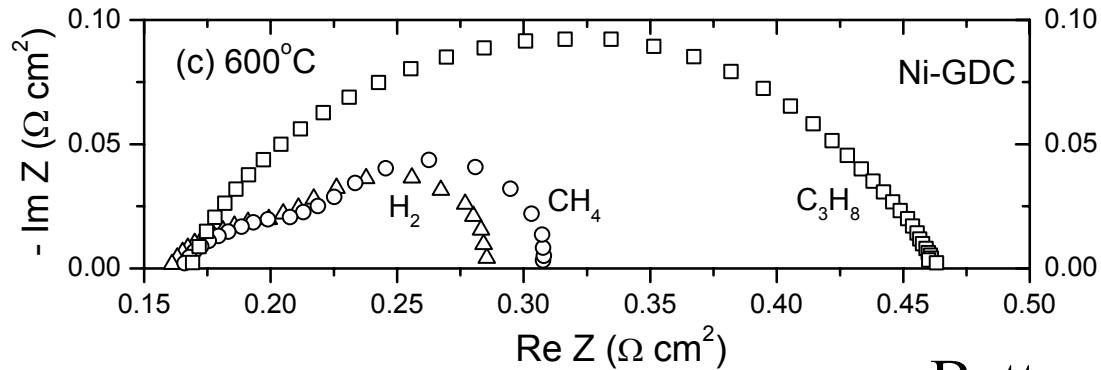
Anodes Fabricated by Impregnation

Cu-GDC

600 °C



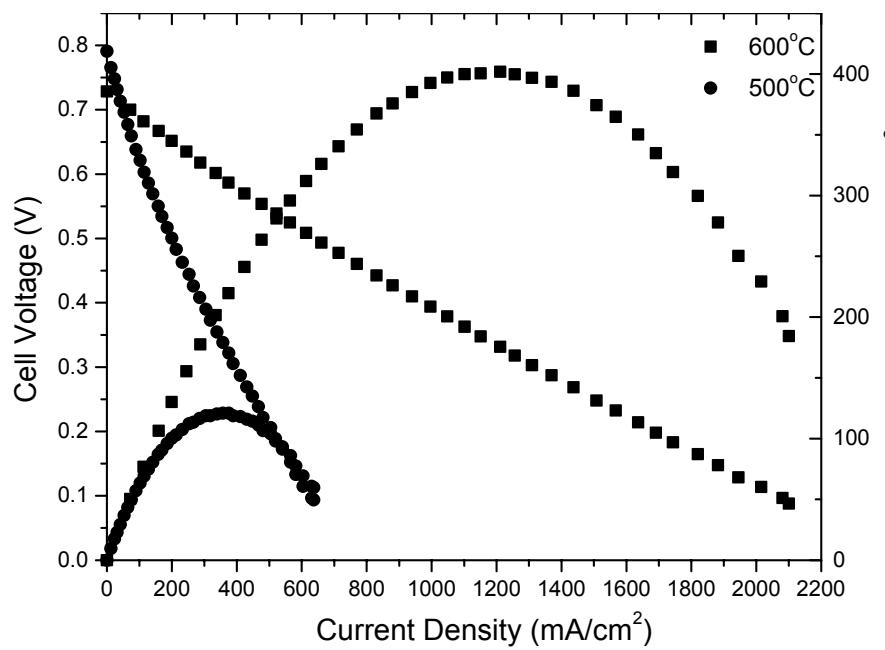
Ni-GDC



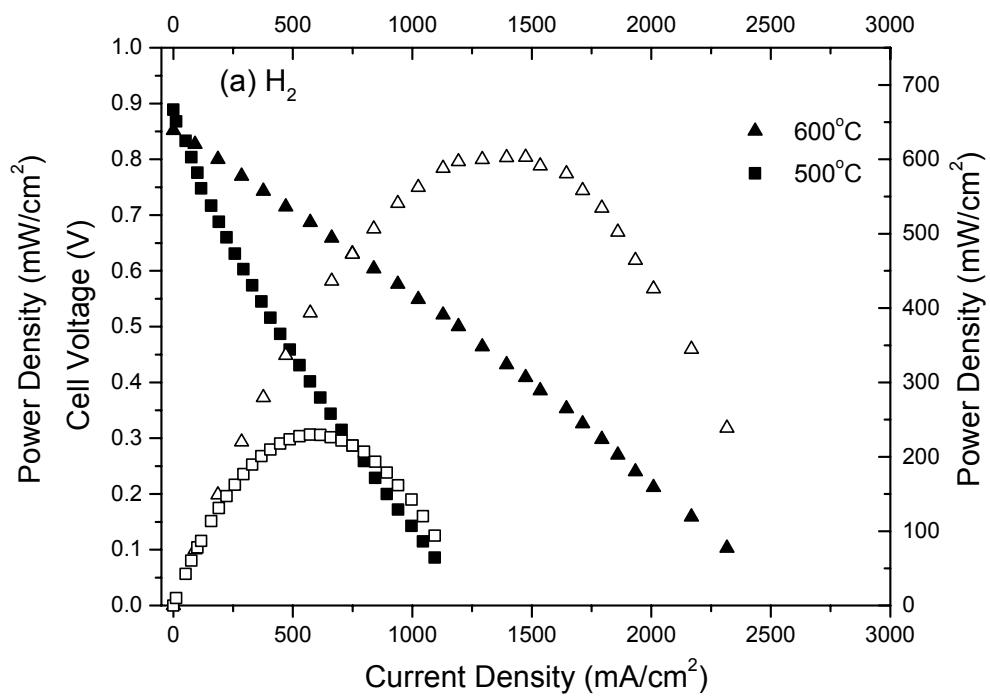
Better Performance

Effect of Fabrication Techniques

Fuel cell performance of Ni-GDC base SOFC



Ni-impregnation



Dry co-pressing Ni-GDC

Summary – Anode Development

- Anode microstructure dramatically influence interfacial resistance, OCV, and power density
- Anodes with finer of NiO and GDC display more than 1 order of magnitude smaller R_p
- A solution impregnation process was developed to fabricate Cu-containing SOFCs
- Direct utilization of hydrocarbon fuels below 650°C
 - Ni-GDC (co-pressing): 519 mW/cm²(CH₄,600°C)
 - Cu-GDC (impregnation): 170 mW/cm²(C₃H₈, 600°C)
- Pre-reforming of higher hydrocarbon may significantly improve SOFC performance

Future Work

- **In-situ Characterization of Reaction Mechanisms Using Raman/IS/MS**
 - Cracking
 - Steam Reforming
 - Sulfur poisoning
- **Modeling of Anode/Electrolyte Interfaces**
 - Optimum Microstructure/Architecture
- **Refine Fabrication of Electrodes with Optimal Microstructures**

Acknowledgements

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